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TIDAL FLATS IN ESTUARINE WATER
QUALITY ANALYSIS

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31 December 1970

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TIDAL FLATS IN ESTUARINE WATER QUALITY ANALYSIS

Research Grant 16070 DGO
Federal Water Quality Administration

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CHAPTER I

INTRODUCTION

General Background.

The following report summarizes the work performed through the first eight months of the second year of a three-year study entitled "Tidal Flats in Estuarine Water Quality Analysis". This study is supported by the Federal Water Quality Administration through Research Grant No. 16020 DGO.

General Approach.

The technical material presented within this report is arranged in logical order rather than in the chronological order that the work was performed. The writer feels that it would be of value however, to briefly discuss the general approach used during the past two years and briefly discuss how this approach often changed the direction of the research.

The general objective of this research is to learn more about the estuarine system and, in particular, the tidal flat system, with particular emphasis given to how man's activities can disrupt these systems to the eventual disadvantage of man. The number of items and relationships occurring within these systems is so numerous and complex that a complete study is essentially impossible. Research effort must be thus directed to study those areas which appear to be of greatest importance. The difficulty is that our knowledge of what we determine to be most important, changes as we learn more about the systems.

This knowledge (obtained from all sources) hopefully indicates new areas which may be of great importance. A research project must be flexible enough to respond to new information yet stable enough to lead to sound results. Lack of flexibility often results in the pursuit of those items which are already known quite well, while lack of stability can often lead to nothing.

In the reported research project, an approach was used in which emphasis was alternately given to mathematical models and experimental results. That is, the experimental results improved the

mathematical models while the models in turn suggested where further experimental results might be most profitable.

As an example, the oxygen demands of tidal flat areas, particularly the benthic deposits, was recognized from the start as an important consideration. First, laboratory studies were made to study the benthic uptake. Next, a simple mathematical model was developed. From this model, an in situ benthic respirometer was designed, built and run. The results from the in situ benthic oxygen uptake rate studies appeared to be affected by leakage from the respirometer. A mathematical model of the respirometer system was developed and, from that model, correction for the leakage was made. The corrected benthic oxygen uptake rates were then studied. The mathematical model results indicated that the experimental results could only be explained if a substantial portion of the measured oxygen uptake rate was due either to the dissolved oxygen, DO, diffusing into the deposits or due to the release of a material which was oxidized rather quickly (half life of several hours or less). Both of these processes suggested that a large portion of the benthic uptake (not including benthic plant respiration) was due to a quickly oxidizing material; the material being oxidized either within the aerobic region of the deposit or within the overlying water. The literature (and common sense) suggested that free sulfides might be such materials. Because free sulfides (particularly hydrogen sulfide) are quite toxic, their presence within the water might often be of greater significance than the low DO values which result, in part, from the oxidation of the free sulfides. It was generally felt at the time, however, that the rapid rate at which free sulfides are oxidized would prevent its presence in waters containing measurable DO. Thus, it was felt, that the free sulfides which were released from the anaerobic regions of the deposit would normally be completely (or near completely) oxidized within the aerobic zone of the deposits. The literature also reflected this notion. A mathematical model of the aerobic zone of the deposits was developed. This model included the downward diffusion of DO, the upward diffusion of free sulfides and the reaction between the two. The model results indicated that under certain conditions, the free sulfide concentrations would likely be significant. Experimental methods were then developed and significant concentrations of free sulfides were measured in certain areas. Field studies and an exhaustive literature review then led to a qualitative description of what appears at this time to be the important processes leading to both the oxygen uptake and the release of free sulfides. A more complex mathematical model is now being developed so as to quantitatively describe these processes. Experiments are now being developed which will hopefully lead to a refinement of the more complex model. Likewise, mathematical experiments (sensitivity studies) with the model will hopefully lead to more efficient utilization of experimental resources.

Already the results (both experimental and mathematical) are indicating how man's activities might effect the tidal flat ecosystem. As an example, a higher percent of silts and clays within the deposit appears to lead to higher sulfide concentrations both within the upper regions of the deposit and within the overlying water. A wide range of activities might lead to a significant increase in the percent of silts and clays.

Detail and Perspective.

The real world appears to be organized into an intergrated series of organizational structures. On an extremely small scale, atoms are organized to form molecules. On a large scale, the planets and sun are organized to form the solar system. Large numbers of intermediate structures, some obvious and some not, are of course present. The definitions of different structures and the disagreements of these definitions will not be pursued. Rather, the point to be made is that a given structure or entity is both made up of components and is also a component of a higher structure.

In order to understand the natural world, man has found it necessary to group what appear to be natural structures into larger groupings. As an example of a functional grouping, individual organisms with similar functions have been grouped into trophic levels. This grouping has enabled man to study the relationships between large groups of organisms. Such a grouping thus enables one to gain perspective, yet because of this larger grouping, one loses detail.

The same real world systems may be studied at a fine level of resolution. That is, smaller groupings may be employed. As an example, individual organisms may be grouped into species. Such groupings permit one to gain detail, yet, because of the larger numbers of groups, one now has great difficulty in gaining perspective.

The point to be made is that the same real world system may be studied at different levels of organization (that is, different levels of resolution; different degrees of grouping). A fine resolution leads to a gain in detail with a sacrifice of perspective while a low resolution leads to a gain in perspective with a sacrifice in detail (precision).

Different investigators (and different professions) often look at the same real world system from different levels of resolution.

Such a varied resolution approach often leads to information concerning both detail and perspective.*

This project, from the start, has studied the tidal flat system (a loosely defined structure having, however, some unique characteristics) from two general views (i.e. at two general levels of organization.) Related component parts which make up the tidal flat system were studied. In addition, the larger estuarine system, of which the tidal flats are components, was also studied.

Feedback occurred between the results gained from the different views; that is, results gained at one level of organization influenced the direction of work done at the other level of organization. As an example, the percent of fine particles within the tidal flat deposits appear to be important as has been previously discussed. This result came from investigating the components of the tidal flat system (fine level of resolution).

A wide range of man's activities might lead to a significant increase in the percent of silts and clays. These activities may be studied at lower levels of resolution; by studying the estuarine-river system. Upstream dams tend to hold back larger particles while suspended particles (colloidal and near colloidal) can proceed downstream. A large portion of these particles may then flocculate and settle out in the more saline estuarine waters.

Dredging operations tend to suspend large amounts of bottom materials. The larger particles settle quickly and are thus eventually picked up by the dredge. The fine particles remain suspended for a longer period of time and thus may be carried by currents far from the dredge. Often, currents at the lower depths within estuaries have a net velocity in the landward direction. Such net landward velocities have been measured within the Yaquina as part of this project. Because of settling, the fine particles stirred up by dredging would tend to concentrate at greater depths and thus they would often be transported upstream with some eventually being deposited on tidal flats.

* Authors Note: Some information may require both detail and perspective simultaneously. Such information may well be essentially unattainable. At this time, however, I will not pursue this rather philosophical question of "ecological uncertainty".

Both the dams and the dredging thus appear to contribute to an increase in the percent of fine material. Jetties and breakwaters may also contribute toward a larger number of fines. The magnitude of the above described processes and their long range consequences is currently only a matter of speculation. Hopefully, the further experimental-mathematical results obtained under this project will contribute toward more meaningful answers.

CHAPTER II

THE TIDAL FLAT SYSTEM

Introduction

In this chapter, components of the tidal flat system and the interactions of these components will be discussed.

DESCRIPTION OF THE TIDAL FLAT SYSTEM

General Description.

The tidal flat deposits of estuaries are areas of extreme complexity and activity. They serve as both sources and sinks of a nearly infinite variety of compounds and materials, produced by equally as many and varied processes. They are in a constant state of material and energy flux with the surrounding environments. Consequently any approach to an understanding of the tidal flat system must involve a study of the biological, chemical, physical and hydraulic factors and processes present within the system.

Based on field research and literature review conducted under this project, a conceptual model of the portions of the tidal flat ecosystem to be discussed herein is illustrated in figure 1. In selecting the level of resolution for which the model of a system is to be developed, one must trade between detail and perspective. Too great a detail makes it difficult to define the relationships between the many components of the model. Sacrifice of detail, however, while leading to better perspective, often eliminates much useful information from the model. The level of resolution shown in figure 1 was chosen to illustrate certain concepts which are believed to be of importance with regard to water quality. Omission of factors from figure 1 should not imply that they are unimportant. As an example, other nutrients (such as nitrogen and phosphorous), detritus feeders, extracellular enzymes, and fungi are among the many factors that play significant roles within the tidal flat ecosystem yet, for the sake of clarity, have not been separately included in figure 1.

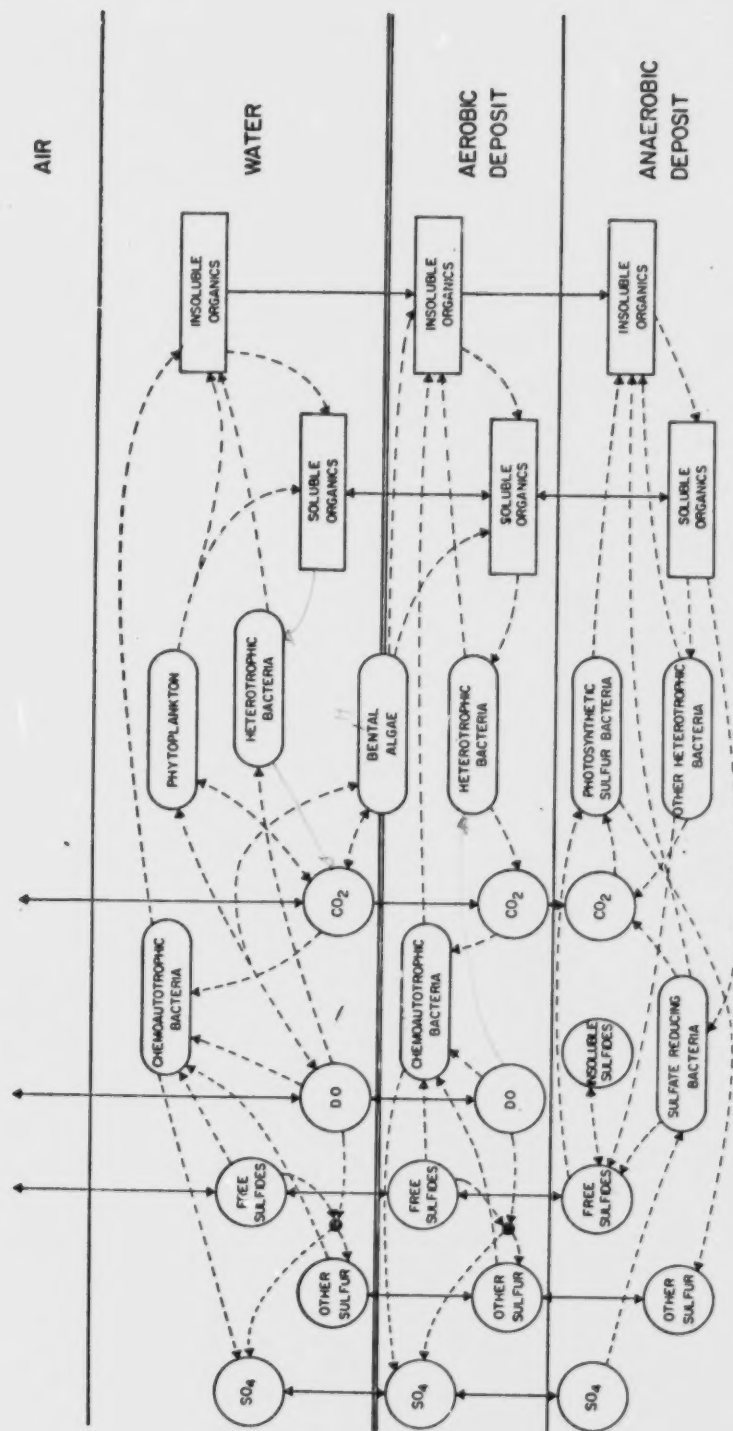


Figure 1/- A Model of the Tidal Flat System.

Test Site Descriptions.

Four principal test sites were chosen for the field portion of this study. Site 1 was located on the south side of Yaquina Bay immediately to the east of the Oregon State University Marine Science Center, Newport, Oregon. This site lies within a mile of the estuary mouth. High salinities, low temperatures, and high tidal current velocities are characteristic of this site.

Site 2 is approximately three miles upstream of site 1 on the east side of the Yaquina estuary adjacent to Parker Slough. Waters here are slightly less saline, have higher temperatures, and lower tidal velocities. Burrowing by benthic invertebrates is extensive, as are mid-summer blooms of the benthic alga, Enteromorpha.

Site 3 is located 14 miles upstream and 300 feet east of the Toledo, Oregon, Yaquina River bridge. A Kraft process paper mill, several sawmills and several log storage areas are located in the proximity of site 3. A major portion of the wastes from the Kraft mill are exported from this area by pipeline to an ocean outfall. The effect of fresh water is evident in the lower salinities, and higher temperatures. Current velocities were comparable to those at sites 1 and 2. Burrowing, however, was negligible.

Site 4 was located on the south side of Isthmus Slough in Coos Bay, Oregon. This site is in a highly industrialized area containing many pulp and paper mills and is located on a mud flat which is partially protected from the main channel currents by an embankment and log storage area. Tidal velocities are low, temperatures are comparable to those at site 3, and salinities range midway between those of sites 2 and 3.

General Procedures.

Sediment cores were collected at each site using plexiglas coring devices, placed in a cooler, and transported directly to the laboratory for analysis. Redox potentials were determined by fixing the cores in a vertical position, placing a reference electrode on the sediment surface, and inserting a 1 mm platinum wire into the core through small holes drilled at appropriate intervals in the plexiglas. The reference electrode used was a standard fiber junction reference electrode used in pH measurements, modified by fastening a fine frit gooch crucible about its tip and filling with saturated potassium chloride solution (3). The large surface area offered by the fritted bottom of the crucible insures proper electrical contact between the probe and the sediment. Measurements of potential were made with a Beckman Expandamatic pH Meter following prior standardization in a solution of known redox potential.

Cores were then extruded into a plexiglas slicing trough and sliced into selected one centimeter-thick sections. Each section was divided into subsamples for determination of total sulfides, volatile solids, and particle size. Total sulfides were determined by a modification of the standard titrimetric method (4). Volatile solids were determined by drying at 105° C and subsequent combustion at 600° in a muffle furnace (4). Volatile solids are reported as a percent of sediment wet weight.

Particle size was determined by a settling tube technique. Separation of the sediment into sand, silt and clay fractions was based upon settling velocities of quartz spheres (5)(6)(7). The settling tube used was designed by Emery (8) and modified by Poole (9).

Plate counts of aerobic bacteria were determined by culturing on marine agar 2216. Most probable numbers of sulfate reducing bacteria were determined on modified SIMS and modified halophilic sulfate reducing media (10).

Dissolved oxygen was measured both by the standard winkler test (4) and by a modification of this test for smaller samples (55).

Physical Factors.

Consider a vertical slice of a typical tidal flat at high tide (see fig. 1). There are two phase boundaries present in this system; the upper boundary (air-water interface) through which gases can pass by transfer processes, and the lower boundary (sediment-water interface) through which soluble compounds may enter and leave the sediment. In addition, two other less distinct boundaries can be defined: the boundary between the upper well mixed turbulent waters and less mixed waters adjacent to the sediment surface (not shown in figure 1), and the boundary between the aerobic and anaerobic regions of the bottom deposit.

Within the water phase, energy may enter the system as light, organic compounds, and inorganics, to be used by photoautotrophs, heterotrophs, and chemoautotrophs, respectively. Light cannot penetrate more than a few mm into the sediment, however, and thus photosynthesis probably does not occur below 5 mm (10)(12)(13). Potential energy in the form of organic matter transported into the flat area or produced through photosynthesis is imported to the sediments from above, by settling and diffusion through the mud-water interface. This energy may be used directly by detritus feeders, but increasing evidence suggests that bacterial and possibly fungal decomposition of this organic matter is necessary for complete utilization by other organisms (14)(11)(15).

Within the sediment, there are two zones based upon the availability of oxygen for energy yielding processes. The upper, or aerobic zone, receives dissolved oxygen from the overlying water by means of vertical mixing. The depth of this aerobic zone depends to a large extent on the mixing within the deposit.

Vertical mixing within a tidal flat deposit depends on a variety of factors. Hydraulic factors, such as tidal changes in water depth, water velocities, wave action and low tide drainage patterns all contribute toward vertical mixing (16)(17). The burrowing and movement of organisms within deposits leads to greater vertical mixing (18)(19)(20). Dye tests at site 2 indicated a large exchange of water through mud-shrimp burrows (21). The presence of fine particles within the deposits tends to reduce vertical mixing (16)(17). A substantial difference in particle size was measured between sites 1 and 4 (see table I). Ebbing waters were found to drain freely through the deposits at site 1 while a lack of such drainage was noted at station 4. Water velocities measured at sites 2 and 3 with a price current meter were generally below 0.6 fps.

The presence of biological growth may retard the passage of water through the deposits and thus reduce the hydraulic tidal mixing. At site 1, permeabilities of 0.04-0.03 cm/min were measured at locations where biological growths were not noted while, in this same general region, the permeability in the top twelve centimeters was reduced to 0.0008 cm/min in areas of noticeable biological growth on the deposit surface.

In regions where vertical mixing is reduced to that of molecular diffusion. The departure from straight-line diffusion, due to the deposit particles, reduces molecular diffusion coefficients by approximately 30 percent from that of pure water (22)(23). Electric interaction between particles and interstitial water can also lead to a reduction of molecular diffusion (24). Diffusion within biological slimes can also be significantly less than diffusion through pure water (25). Vertical mixing can thus be expected to vary from relatively large hydraulic exchanges, often facilitated by burrowing organisms and large particle sizes (site 1), to values less than that of molecular diffusion in pure water (possibly the case at site 4).

Care must be exercised in the use of reported molecular diffusion coefficients of substances within interstitial water, as the concentration of sorbed material which does not diffuse is often included with the material in solution (24). Concentration gradients based on the sum of sorbed and nonsorbed materials will lead to lower

Table I. - Comparison of Particle Size at Sites 1 and 4.

Depth	SITE 1		SITE 4	
	Sand (a)	Silt and Clay (b)	Sand (a)	Silt and Clay (b)
0- 1 cm	92.2	7.8	2.9	97.1
2- 3 cm	99.3	0.7	1.3	98.7
4- 5 cm	87.6	12.4	0.6	99.4
7- 8 cm	93.1	6.9	2.3	97.7
11-12 cm	95.3	4.7	3.9	96.1

(a) Particles larger than 63μ .

(b) Particles smaller than 63μ .

calculated diffusion coefficients than if only the material in solution were used to determine the gradients.

The reducing conditions of the sediments determine, and are in large part determined by, microbial processes. Within the anaerobic zone, redox potentials are usually quite negative and in some areas have been reported as low as -500 mv (6). Such low extremes are probably due to the presence of hydrogen but are exceedingly rare. No such low extremes were measured at any of the four test sites. More commonly, negative potentials fall between -100 and -250 mv and it is generally recognized that such potentials are primarily due to the presence of sulfides (11)(26)(27)(28). The data shown in figure 2 illustrate the apparent relationship between redox potential and sulfides measured at site 1.

Positive redox potentials within the deposits were not measured at site 4, even though supersaturation of dissolved oxygen within the overlying water during the daytime was common, thus, indicating that the oxidized layer of the mud was extremely thin. The greater depth of the aerobic zone, as determined by the greater depths of positive redox potentials found at site 1 compared to site 4, is largely due to the greater mixing at site 1. Greater water velocities, larger particle sizes, better drainage and more burrowing by macroorganisms at site 1 contributed to this greater mixing. Figure 2 also illustrates the variations one can expect within tidal deposits at different levels of exposure. In particular, the high redox potentials and low sulfides at elevation 5.6, reflect the effects of extensive shrimp burrowing found at that level.

Drainage of Tidal Flat Pore Water.

During August and September of 1970, a series of experiments were conducted at sites 1 and 3 in order to study the discharge and recharge process of tidal flat pore water during a tidal cycle.

During the first series of experiments at site 1, measurements of the hydraulic surface within the flats were obtained by means of pipes driven into the deposits. It was found, however, that the hydraulic response of the system was too slow. During later investigations, the hydraulic surface was measured through dug holes with the surface referenced to stakes of known elevation. Changes of the hydraulic surface for three stations located at site 1 are shown in figure 3. The station elevations are shown on figure 4 and the free water surface elevations, which were measured during the sampling period shown on figure 5.

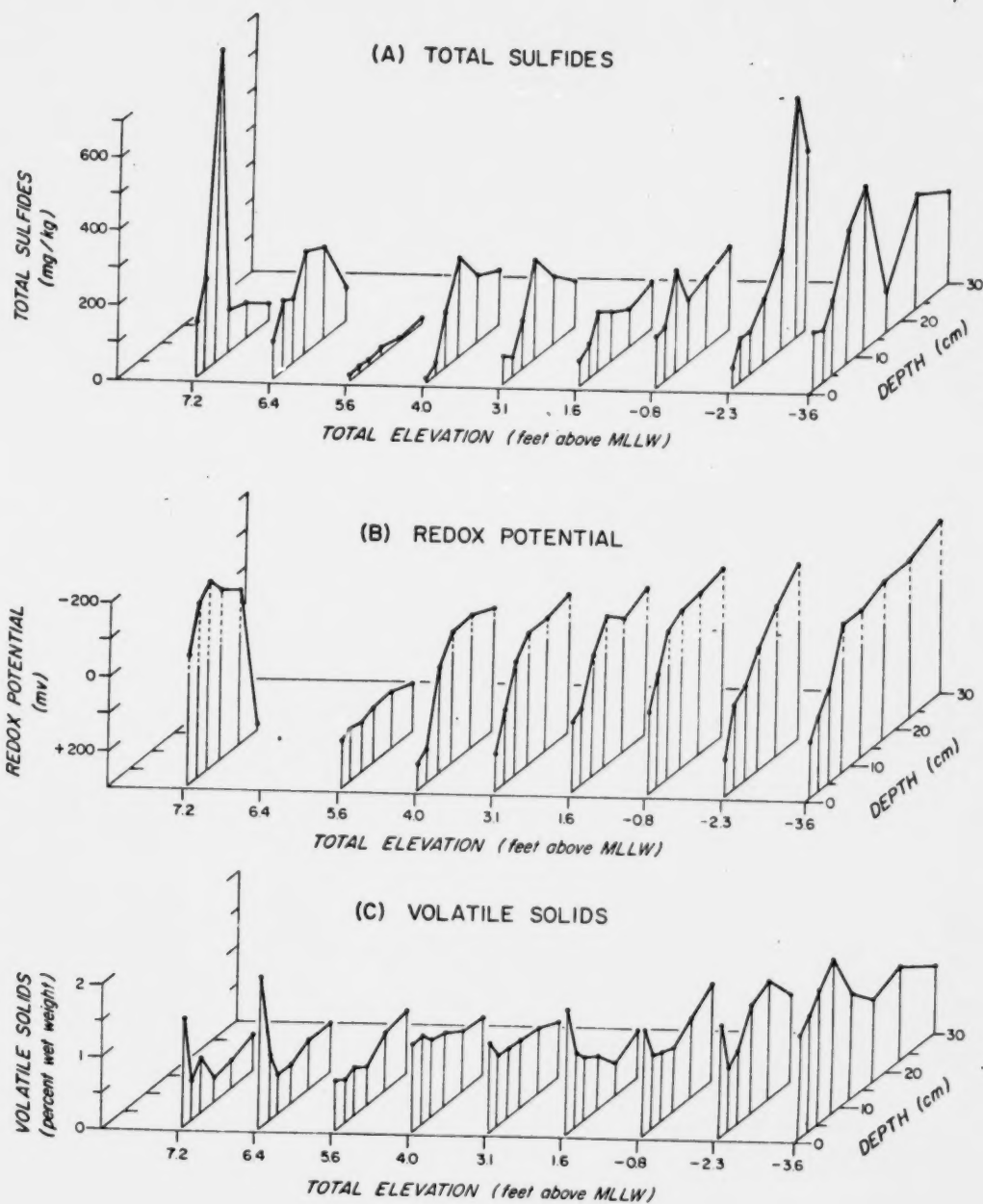


Figure 2 - Measurements of Total Sulfides, Redox Potential and Volatile Solids Within the Deposits at Site 1.

These results suggest that during the ebbing of the tide, pore water drains from those areas exposed by the tide. Drainage is along the beach, passing through the surface at the region above the free water surface. The slope of the hydraulic surface at approximately 2 hours after low tide is shown on figure 4. As seen in this diagram, the hydraulic surface meets the ground surface between stations C and D. Similar hydraulic surface profiles can be drawn for different times within the tidal cycle from the data given in figure 3. Thus, the data shows that the flow of pore water during the ebbing tide and during the low tide period results in a surface flow component at different elevations at different periods of the tidal cycle. The magnitude of this surface flow component will depend on the permeabilities found at each location (see figure 6). During the tidal cycle, the hydraulic surface within the flats dropped by approximately 1.5 to 0.5 feet, the larger drops being measured at the higher elevations. Above the hydraulic surface, the water content was reduced to approximately 90 percent saturation. These percents, shown in figure 7, should only be considered as rough approximations due to the difficulty of obtaining undisturbed one inch thick samples.

Using the mixing length description of the diffusion coefficient, the data presented above can be utilized to compute rough estimates of the effective diffusion coefficients due to the tidal pore drainage described above. These effective diffusion coefficients are approximately 10 to 50 times greater than molecular diffusion coefficients (for oxygen) in water. In addition, oxygen may be introduced in large amounts to the unsaturated region.

At site 3, no similar tidal drainage could be measured. Water would remain within pools (with some evaporation) until the flood tide covered the flats. Vertical mixing was thus reduced to molecular diffusion and the turnover by organisms within the deposit. (This later method did not appear to be substantial at site 3). Partial scour of the region was also noted, due to wave action as the tide rose and fell.

The characteristics of the deposits at sites 1 and 3 were quite different (see figures 8 and 9). The deposits at site 1 contained a reasonably uniform sand while large amounts of silts and clays were present at site 3. It appears that the difference in particle size was chiefly responsible for the differences in drainage characteristics and thus the differences in vertical mixing.

During the flood tide at site 1, the hydraulic surface began to rise slowly as the free surface approached a given elevation. (see figure 3). This rise became abrupt at each location as the flooding waters covered that location.

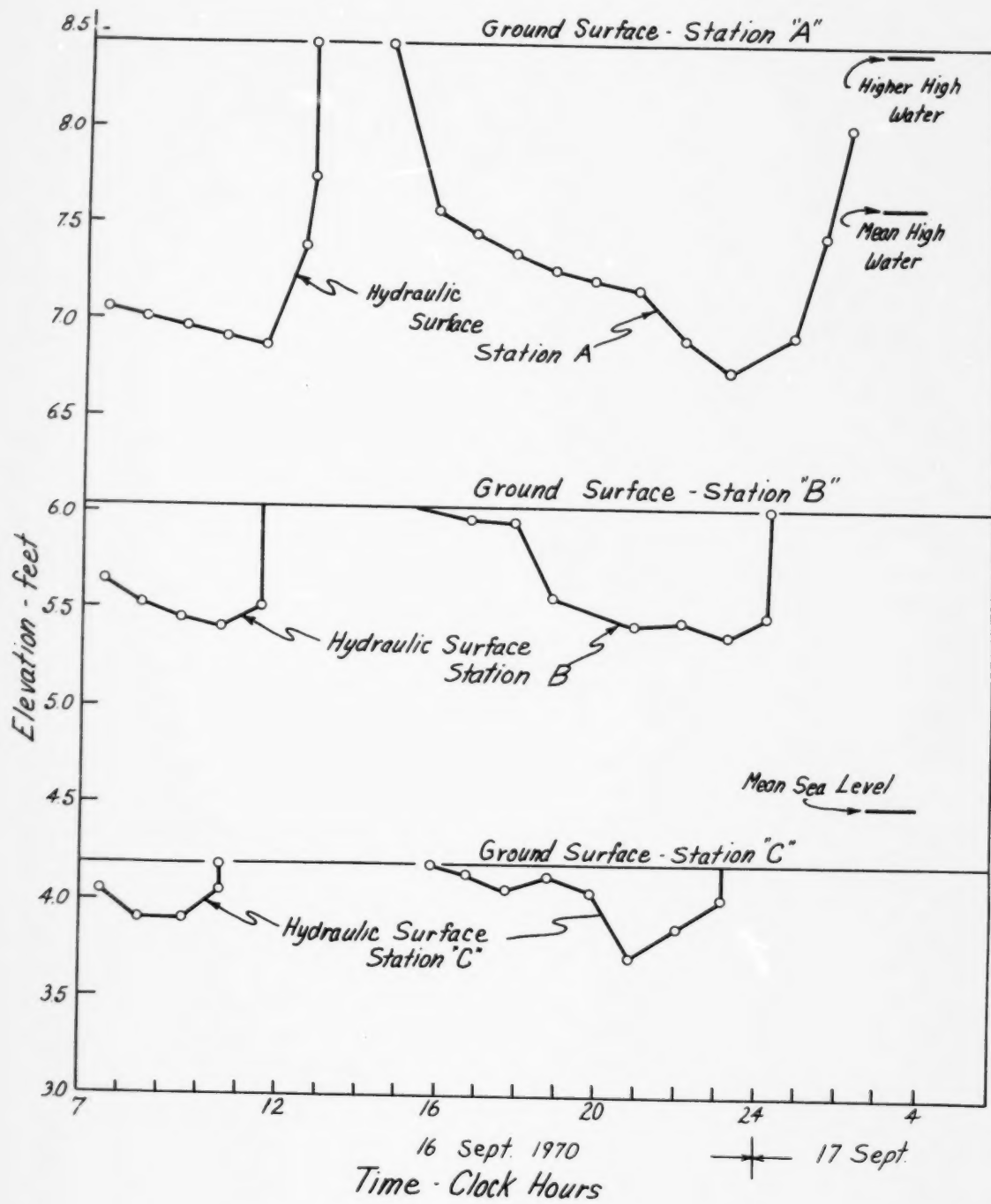


Figure 3 - Variation of Hydraulic Surface with Time

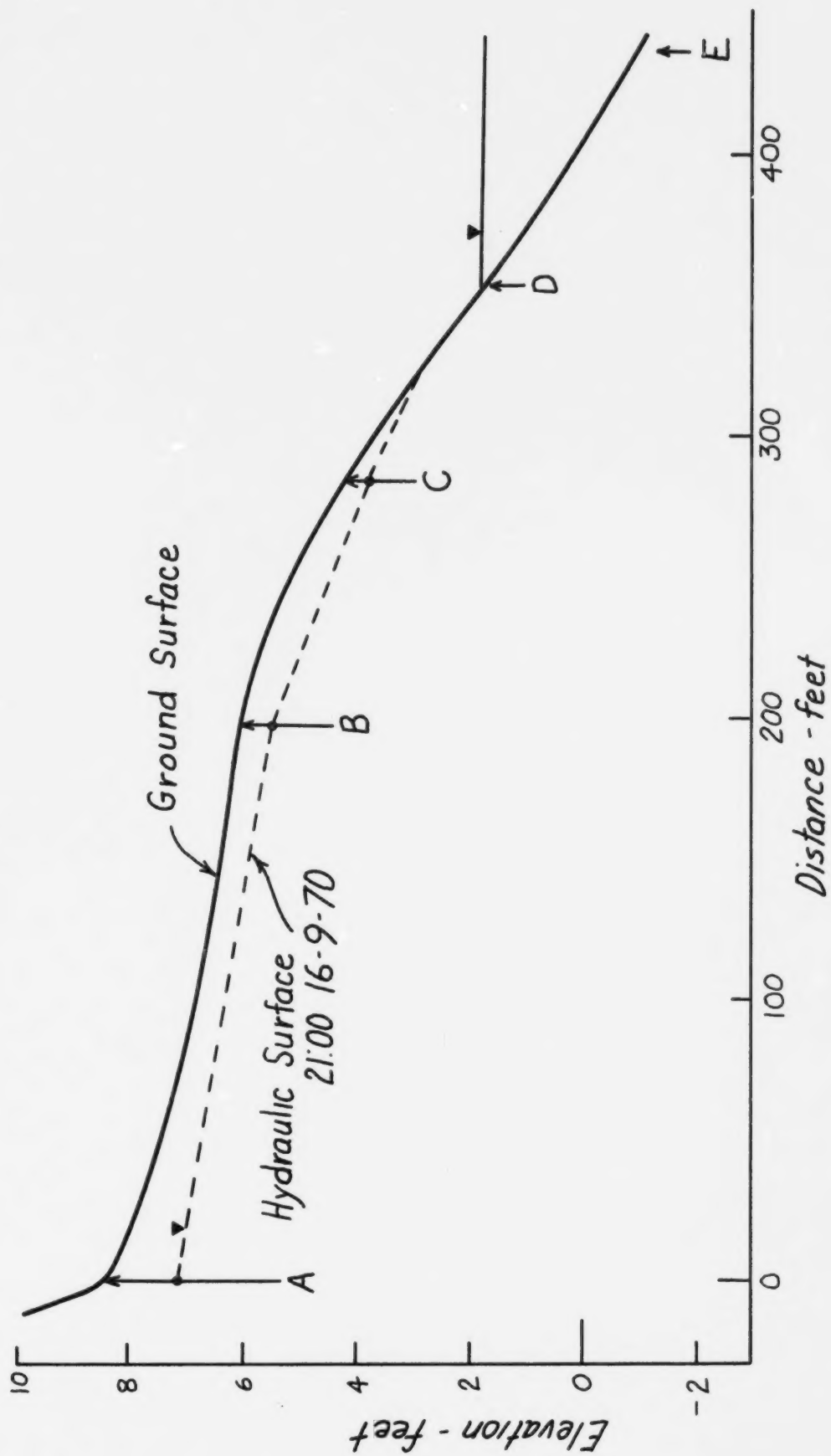


Figure 4 - HYDRAULIC SURFACE, Site 1

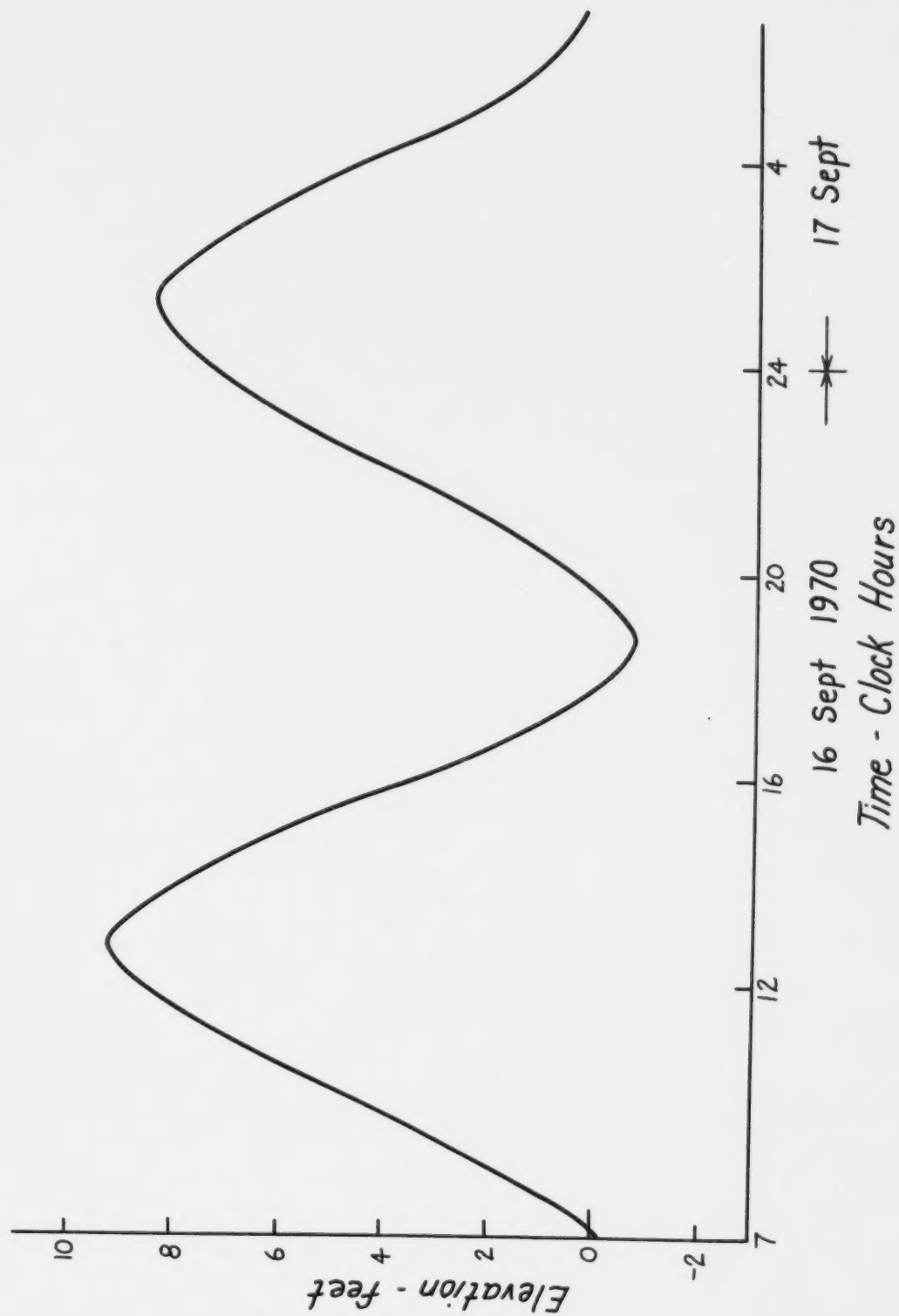


Figure 5 - Tidal Elevations during Drainage Study

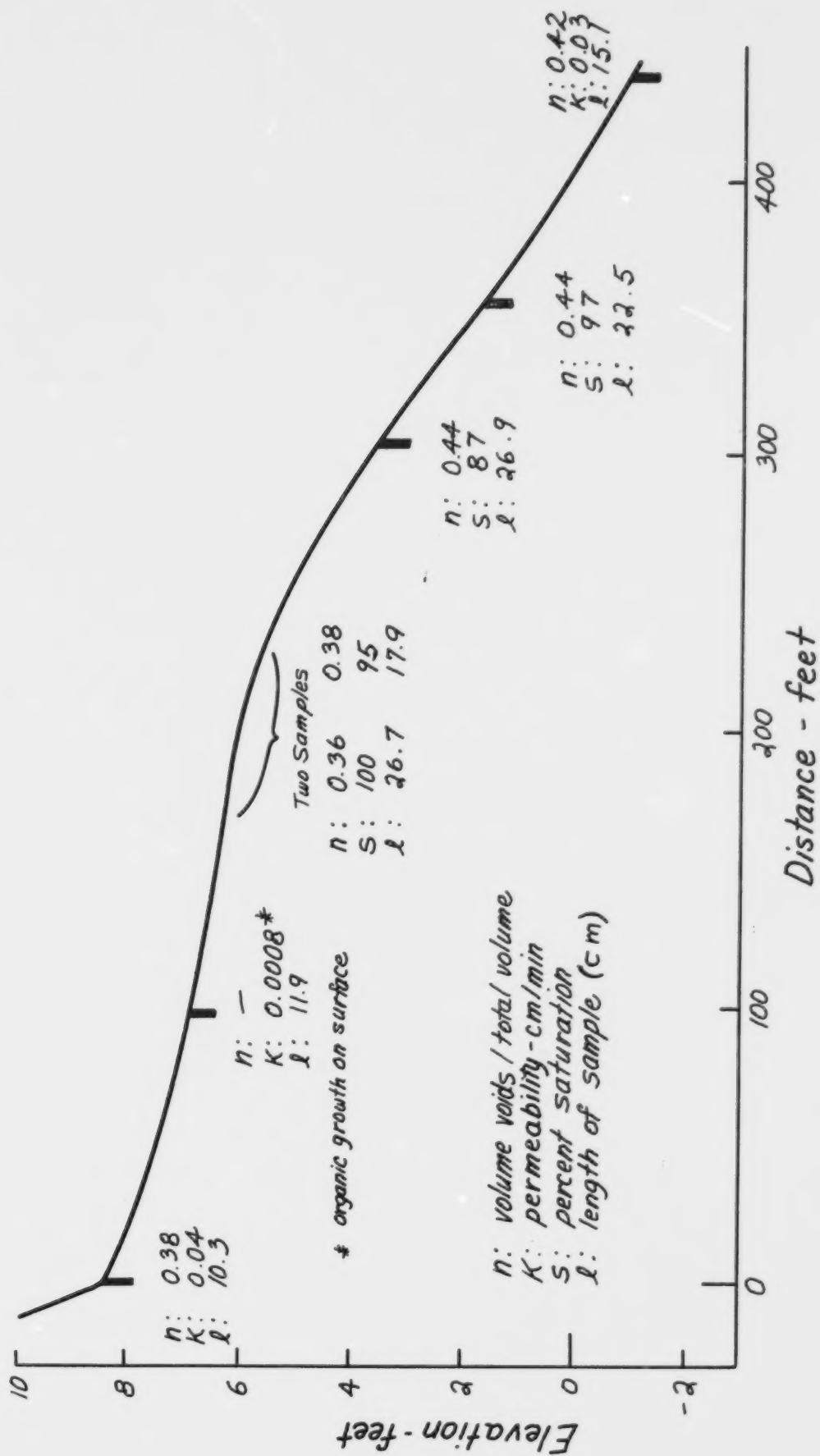


Figure 6 - SEDIMENT CHARACTERISTICS, Site 1

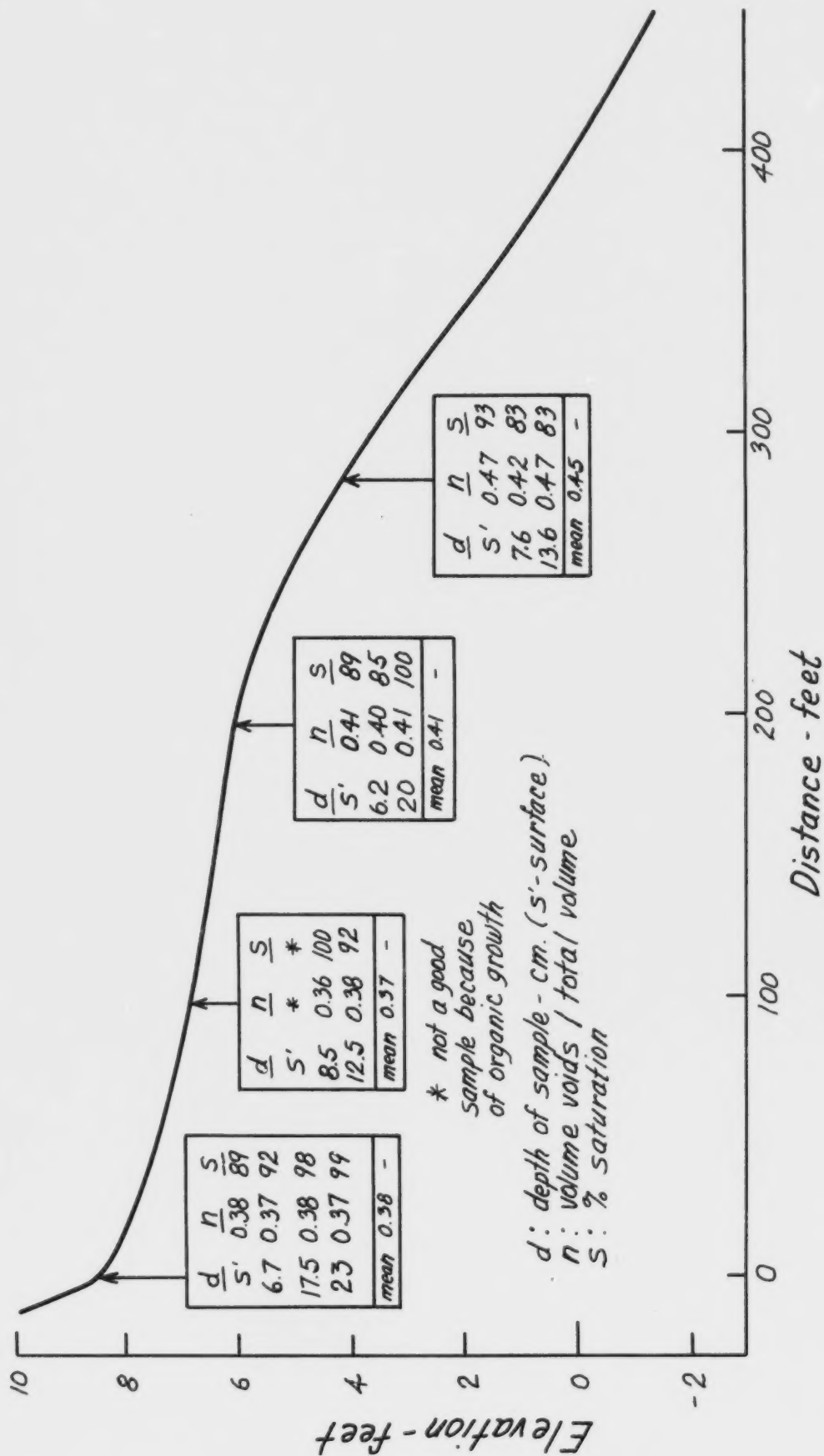


Figure 7 - SEDIMENT CHARACTERISTICS, Site 1

Figure 8 - GRAIN SIZE ANALYSIS, Site 1

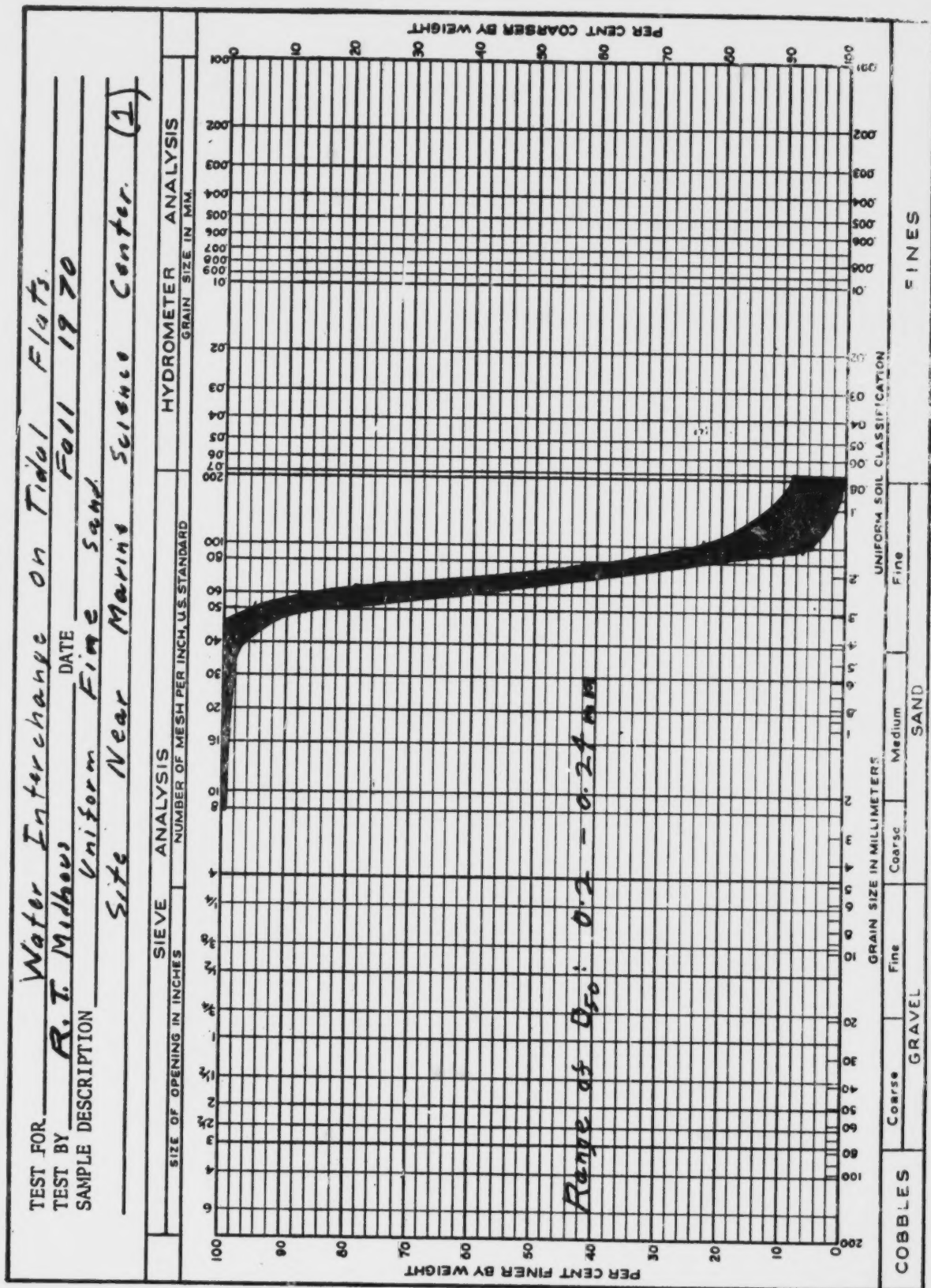
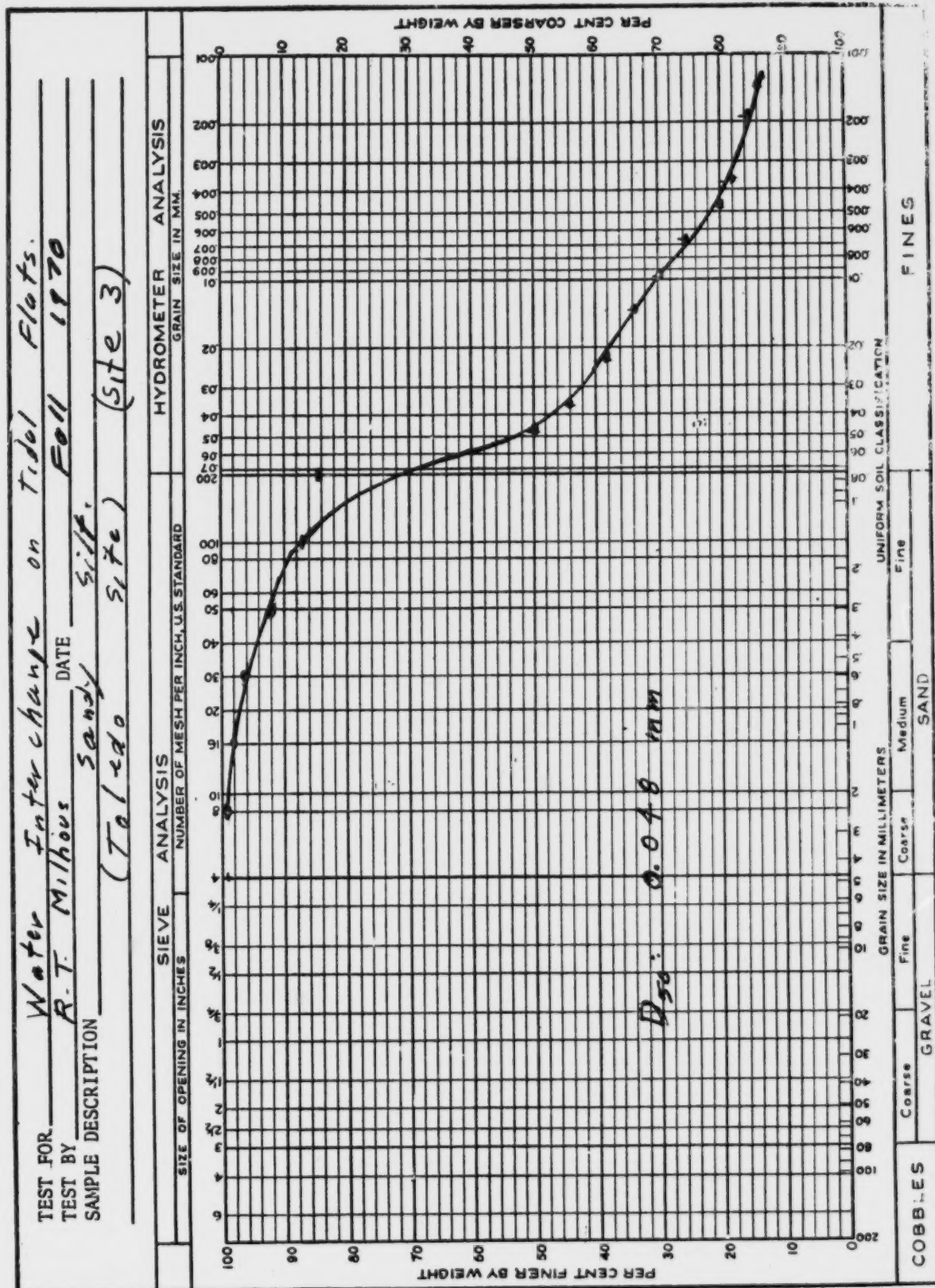


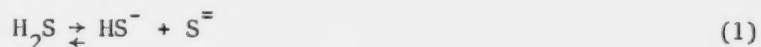
Figure 9 - GRAIN SIZE ANALYSIS, Site 3



Sulfides.

The sulfur cycle has been described in some form in nearly every textbook on ecology. Its importance in intertidal sediment ecosystem has been stressed (11)(26), yet, it has most often received only superficial attention. Various sulfur compounds occur within the water column overlying tidal flat deposits. In most brackish water which is oxygenated, these are usually in an oxidized state, with sulfates being the most abundant. Those sulfur species which are soluble may diffuse across the sediment-water interface and enter the sediments. Within the water and upper aerobic layer of the deposits, inorganic sulfur compounds may be utilized by sulfur oxidizing bacteria, such as those belonging to the genus Thiobacillus, which produce sulfates.

Hydrogen sulfide occurs in aqueous solution as part of the pH dependent system



At a pH of approximately 6.5-7, free sulfides are equally divided between H_2S and HS^- with $\text{S}^{=2}$ being negligible. In the following discussion, components of equation 1 will be referred to as 'free sulfide'. Free sulfide originates within the anaerobic layer where it is primarily produced by heterotrophic sulfate reducing bacteria which utilize the sulfates as hydrogen acceptors (26). When sulfates are available, as is the case for the saline and brackish waters studied for this project, stabilization will likely occur through sulfate reduction rather than through methane fermentation (29).

A summary of counts of sulfate reducing bacteria and total bacteria measured at the four test sites are presented in Table II. Due to the high variability existing within samples, low confidence must be given to absolute numbers. Relative values, however, do indicate distinct trends between sites, with site 4 having the highest counts of both total and sulfate reducing bacteria.

Free sulfides may also be produced during anaerobic putreficiation of sulfur containing amino acids, but this process is felt to be of lesser importance in the marine environment (28)(11). The fate of the free sulfides thus produced will depend upon the physical and chemical characteristics of the deposits. If sufficient amounts of metal ions, such as iron, are present, the sulfide will form insoluble precipitates. If removal of these insoluble sulfur compounds does not take place, either by resolubilizing or through transport out of the area, the levels of total sulfide, which include free, soluble, and insoluble forms, may reach significant proportions in the sediments (figure 2 and Table III).

Table II. - Bacterial Counts Per Gram of Wet Sediment

Location	Depth	Total Plate Count ^(a)	Sulfate Reducing Bacteria ^(b)
Site 1, 3.1 ft. MLLW	0- 1 cm ^(c)	6.3×10^6	3.6×10^2
	2- 3 cm ^(c)	4.7×10^5	7.3×10^2
	4- 5 cm ^(c)	1.5×10^5	3.6×10^2
	10-11 cm ^(c)	4.5×10^4	300
Site 1, -2.3 ft. MLLW	0- 1 cm ^(c)	5.5×10^6	4.8×10^3
	2- 3 cm ^(c)	1.2×10^6	4.2×10^3
	4- 5 cm ^(c)	1.2×10^6	5.7×10^3
Site 2	0- 1 cm ^(c)	6.5×10^6	4.7×10^4
	10-11 cm ^(d)	3.5×10^5	1.3×10^4
	20-21 cm ^(d)	4.2×10^5	1.7×10^3
	27-28 cm ^(d)	1.1×10^5	1.3×10^3
	30-31 cm ^(d)	1.2×10^5	1.8×10^3
	35-36 cm ^(c)	4.4×10^4	2.8×10^2
Site 3	0- 1 cm ^(f)	3.7×10^6	1.2×10^5
	10-11 cm ^(f)	2.9×10^5	6.7×10^3
	20-21 cm ^(f)	1.9×10^5	4.2×10^3
	30-31 cm ^(e)	2.6×10^5	8.8×10^3
Site 4	0- 1 cm ^(c)	1.4×10^7	2.5×10^5
	2- 3 cm ^(c)	2.5×10^6	3.4×10^4
	4- 5 cm ^(c)	1.4×10^6	4.6×10^4
	7- 8 cm ^(c)	7.9×10^5	8.4×10^3
	11-12 cm ^(c)	2.2×10^5	6.8×10^3

(a) On marine agar 2216 (numbers per gram of wet sediment)

(b) MPN using modified SIM medium or a modified medium for halophilic sulfate reducing bacteria (10). (numbers per gram of wet sediment)

(c) Determined on 1 date

(d) Average on 2 dates

(e) Average on 3 dates

(f) Average on 4 dates

Table III. - Core Analysis for Total Sulfides and Volatile Solids at Sites 3 and 4

Depth (cm)	SITE 3		SITE 4	
	Total Sulfides(a)	Volatile Solids(b)	Total Sulfides(a)	Volatile Solids(b)
0- 1	116	7.03	188	3.98
2- 3	330	5.26	1614	3.89
4- 5	1400	5.43	1947	4.18
7- 8	1200	6.80	870	5.76
11-12	1120	7.41	1013	5.88
(a) as mg sulfide/kg sediment				
(b) precent wet weight of sediment				

If the aerobic layer of the sediment is thin enough to allow light to penetrate to the anaerobic zone, photosynthetic purple and green sulfur bacteria may utilize the sulfides as hydrogen donors, producing free sulfur as a by-product. This often occurs below a layer of benthic algae, and is possibly due to the lower compensation point for photoreduction, and to the ability of the photosynthetic bacteria to utilize longer wavelength light than the algae (11)(30). At site 4, a light purple color, believed to be caused by the presence of purple sulfur bacteria, was noticeable on portions of the mud surface and immediately below mats of benthic blue-green algae which covered large portions of the site. The purple growth was identified as belonging to the purple sulfur bacteria, but as yet has not been classified as to genus. The identification was based upon the growth of the organism under anaerobic conditions with exposure to light. Simple methylene blue stains and wet amounts of the purple growth found on the sediment surface and colonies grown on the inorganic salts agar resembled the general description of

purple sulfur bacteria (31). The medium used for isolation and identification was an inorganic salts agar containing Na_2S (31)(32). No similar coloration (light purple) was observed at the three other test sites.

If the rate of sulfide production exceeds the rate at which it can be converted to nondiffusible forms, such as ferrous sulfide or insoluble sulfur, it may diffuse upward into the aerobic region and possibly into the water column. Here it will be oxidized to sulfites, sulfates, thiosulfate, or insoluble sulfur (28)(33)(34).

The chemical reaction of sulfides with oxygen in aqueous solutions has been studied by many investigators. Half lives of free sulfides ranging from 15 minutes to 70 hours have been reported (28)(33)(34)(35)(36)(37). Several studies have described the oxidation of free sulfides to occur by a second order reaction (28)(33)(34), however, such a description is a simplification of an extremely complex system (34). Studies done in sea water have indicated that pH, temperature, and initial oxygen and sulfide concentration are all factors affecting the rate of oxidation (28)(33). One recent study, using distilled water, reported a half life of sulfide of about 50 hours at an oxygen concentration of 25.6 mg/L (34). This study noted that the oxidation is catalyzed by the presence of metallic ions such as Ni, Mn, Fe, Ca, and Mg and is accelerated by some organic substances such as formaldehyde, phenols, and urea. These results suggest that oxidation of free sulfides in estuarine water may be more rapid than in distilled water due to the presence of catalysts. During the past grant period, several experiments were conducted to investigate the rate of sulfide oxidation using aged, 0.2 micron-filtered sea water (salinity of 33 parts per thousand and initial pH at 8.2). Sulfide was measured with a sulfide membrane electrode on samples withdrawn from the system and fixed with a sulfide antioxidant buffer solution. While results varied with initial concentrations of oxygen and sulfide, half lives ranged from 10 minutes to one hour. These limited results are in fair agreement with other studies done in sea water in which half lives in the range of approximately 15-25 minutes were reported (33)(28)(37).

Under conditions of very high release, some hydrogen sulfide may escape into the air creating a nuisance and possible health problem (33). The typical H_2S odor was quite strong at site 4. The release of sulfides into overlying water can have an undesirable effect on water quality. Not only do sulfides exert a demand on the dissolved oxygen, but they have also been shown to be quite toxic at low concentrations to fishes, crustaceans, polychetes, and a variety of benthic microinvertebrates (38)(11)(39)(40)(41)(42)(43)(44)(45)(37). Often the initial free sulfide concentrations present in a batch test in which a given toxic effect was noted have been reported as the concentrations which produce a toxic effect. Because of the

relatively short half life of free sulfides within oxygenated natural waters, these initial concentrations may be considerably higher than the average concentrations throughout the test period. Recent studies have been made in which relatively constant hydrogen sulfide concentrations below .075 mg/L (pH 7.6-8.0) have been found to be significantly harmful to rainbow trout, sucker and walleye, and particularly to the eggs and fry of these fish (38).

Oxygen.

Because of the many processes in which it participates, oxygen is probably the most important factor affecting the structure and functioning of the tidal flat ecosystem. All aerobic life is dependent upon the utilization of oxygen as a hydrogen acceptor, and the vertical zonation of the bottom deposits is a result of the supply of oxygen and light.

In addition to DO imported by water movement, oxygen may be added to the overlying water by two principal processes: reaeration, and photosynthesis. Reaeration is a physical process resulting in the transport of oxygen across the air-water interface, and has been studied in detail by many investigators (46)(47)(48)(49). In tidal flat regions, wind and wave action will have a major influence on the air-water transfer of dissolved oxygen. This transfer may occur either into or out of the water, depending upon the relative partial pressures of oxygen on each side of the interface.

During daylight hours, oxygen is produced photosynthetically by planktonic and benthic green plants through photolysis of the water molecule. The extent of photosynthesis depends on light, nutrients, temperature, and standing crop. During the night hours, photosynthesis ceases, but respiration continues, resulting in a nocturnal decrease of DO. Diel DO variations between 14 mg/L and 6 mg/L were not uncommon at all of the sites. Wider diel ranges of DO were measured at sites 2 and 4.

The diurnal oxygen method has been frequently used to estimate reaeration, photosynthesis and total community respiration. During the past grant period, a review of this method as used by many investigators was conducted. It was found that many investigators failed to indicate how well the actual field conditions corresponded to the mathematical assumptions. In particular, the assumption of complete mixing within the water body under investigation was often not justified. Also, it was often assumed that respiration remained constant throughout the night. Respirometer studies conducted under this project, however, indicated a decrease of respiration with time. Such an error can often lead to an over estimation of reaeration.

Data from the literature did seem to indicate that maximum reaeration rates (transfer coefficients) were higher when measured by the diurnal oxygen method than when measured by other methods. A more theoretically sound approach to the diurnal oxygen method has been developed during the last grant period. A more critical analysis of the diurnal oxygen method will be completed during the next grant period.

The DO uptake of benthal deposits has been studied both in the field (21)(50)(48)(49)(51)(52)(53)(54) and in laboratory systems (55)(56)(57)(58)(59)(18)(60)(20)(62)(63). Benthal oxygen uptake rates were measured at the four sites using in situ benthal respirometers. The results are separately discussed within this report.

Sulfide Release.

The release of materials from the deposits which exert biological and chemical oxygen demands in the overlying water, and the removal of DO from the overlying water into the deposits to satisfy the biological and chemical oxygen demands within the deposit, all contribute to the total benthal oxygen uptake. Sulfides have often been considered as a major contributor to such chemical oxygen demand. The high reaction rate between free sulfides and dissolved oxygen in estuarine waters has contributed to the general assumption that free sulfides released from the anaerobic layers of the deposit will be essentially completely oxidized within the aerobic layer of the deposit. Significant concentrations of free sulfides within waters containing normal dissolved oxygen concentrations has been generally considered as a transient condition due to dredging, scour, or other similar major benthal disruptions. In general, the continued presence of significant concentrations of free sulfides in waters containing dissolved oxygen has been considered improbable. Because of the relatively high toxicity of free sulfides, principally H_2S , the presence of free sulfides might often be a more serious water quality problem than the lower DO values resulting from the oxidation of the sulfides. In the following sections, a quantitative model of sulfide release is developed in order to study the conditions under which significant concentrations of free sulfides in waters overlying sediments, particularly tidal flat sediments, would be possible.

STUDIES OF BENTHAL OXYGEN UPTAKE

General.

During the early stages of this project, a series of laboratory tests were conducted to determine the oxygen uptake rate of deposits removed from site 3. Mud cores were obtained by inserting 3-inch plastic tubes into the deposit. The tubes, with the deposit, were removed to the laboratory where tests were conducted within the same tubes to determine the benthic oxygen uptake.

These early tests determined an oxygen uptake rate of 1.9 gm/m^2 -day under conditions of low mixing and an uptake rate of 3.5 gm/m^2 -day under conditions of high mixing. From these results, an in situ benthic respirometer was developed.

Experimental Design and Procedure.

Light and dark benthic respirometers developed during this research were constructed from plexiglas half cylinders, 5.64 meters long by 0.152 meters wide. The resulting long and narrow respirometer covered a benthic area (0.813 m^2) large enough so that small isolated inconsistencies in bottom muds would not cause great variabilities in uptake rates. The long, narrow shape was also required for simulation of actual mixing conditions. In the respirometer designed during this project, velocities typical of a specific test site were generated over bottom muds by recirculating water in the enclosed long respirometer. A flow development section was constructed on the inflow end of the respirometer to distribute the flow evenly over the respirometer cross section. With the volume to area ratio used, reasonable oxygen uptake rates could be measured in four to eight hours. Removable flanges were designed so that the flange portion of the respirometer could be inserted into the bottom deposit some time before the actual respirometer sections were attached. In this way, the bottom deposit was allowed to come to equilibrium before attaching the respirometer sections, pump, and sampling hoses. The respirometer sections were made in about 4-1/2 foot lengths and could be installed on the preset flanges at low water. Rubber gasket material sealed all joints between flanges and respirometer sections. Water was recirculated in a 1-1/4 inch PVC pipe using a 1/4 hp submersible impeller-type pump. A 1-1/4 inch brass gate valve regulated pump discharge and therefore the velocity within the respirometer.

The respirometer was attached to the preset sealing flanges at low tide and a typical sampling run was conducted during the time that the area was covered with water within a tidal cycle. Samples,

20 ml in size, were brought to the surface and analyzed in the field for dissolved oxygen using a "Micro-Winkler" modification of the Standard Winkler-Azide method. DO, temperature and salinity were measured both inside and outside of the respirometer. The water removed for the samples was replaced with estuary water through a one-way valve which allowed water to flow only into the respirometer as samples were extracted. The displaced volume for all samples on the longest run was less than 4% of the total respirometer volume. Temperatures were taken in place with thermistors inside and outside the respirometers. Figure 10 shows a detailed diagram of the benthal respirometer.

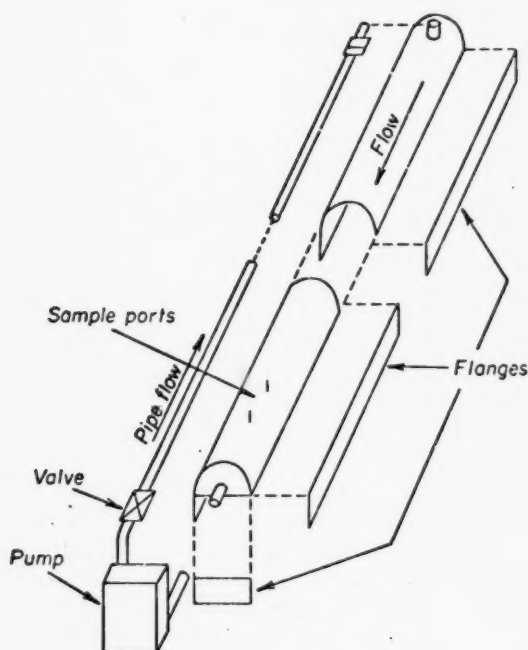


Figure 10. - Large Benthal Respirometer.

To measure the amount of oxygen uptake due to free-floating organisms in the bay-estuary water, planktonic respirometers were developed. Light and dark planktonic respirometers were constructed

of three inch diameter plexiglas tubes, six feet in length. A small submersible impeller pump was attached to one end, and water was recirculated through the tubular respirometer body at approximately 0.2 feet per second. Exterior hose arrangements used to recirculate the enclosed water were constructed so that the hose could be brought to the water surface for sampling. Methods of dissolved oxygen sampling and analysis were the same as those used for the benthal respirometers.

During the second grant year, a simpler benthal respirometer was also developed and used. This simplified respirometer had attached flanges, was 4 feet long and had a small recirculation pump not capable of producing the higher velocities possible with the large respirometer. Both light and dark respirometers of this type were developed. It was intended that the simpler design of this respirometer would make sampling easier and thus facilitate more runs.

Tests indicated that only seven to eight percent of the visible light was obstructed when passing through the 1/8-inch thick plexiglas from which the respirometers were constructed.

Mathematical Model of Benthal Respirometer System.

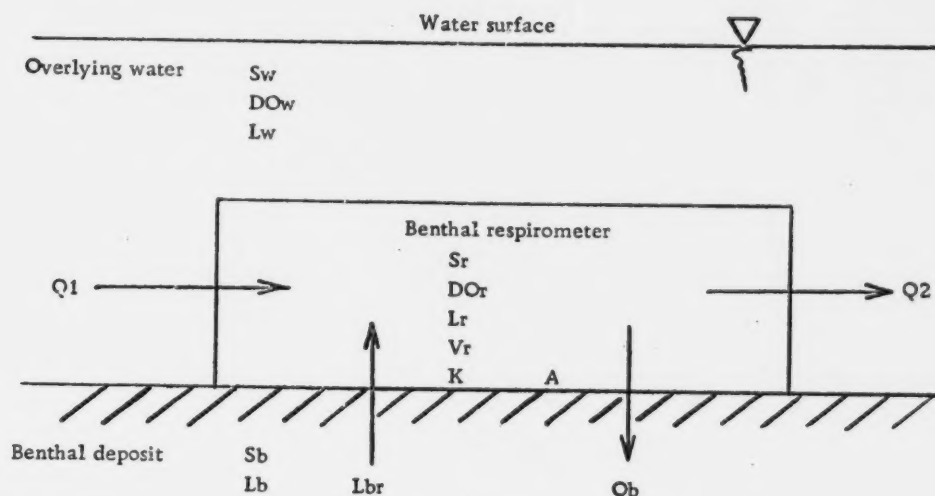
To more thoroughly explain and analyze the results of the respirometer study, a mathematical model of the benthal respirometer system was developed. During the early benthal respirometer runs, excessive leakage was evident at site 2. The leakage was found to be principally caused by extensive mud shrimp burrow activity. A mathematical simulation and leakage correction model became a necessity for evaluating leakage as well as helping to determine the importance of different mechanisms or processes of benthal DO uptake. The model was applied to all test runs where salinity data were taken, and corrected DO uptake rates were calculated where leakage existed. Salinity data were used to evaluate leakage rates.

A schematic diagram of a benthal respirometer system is shown in figure 11 with an explanation of terms used. The mass balance concept is shown by the following expression.

$$\left(\begin{array}{l} \text{Rate change of sub-} \\ \text{stance mass within the} \\ \text{respirometer volume} \end{array} \right) = \left(\begin{array}{l} \text{Rate of substance} \\ \text{input into the} \\ \text{volume} \end{array} \right) - \left(\begin{array}{l} \text{Rate of sub-} \\ \text{stance output} \\ \text{from the volume} \end{array} \right)$$

(2)

From figure 11 and equation (2), one obtains the following:



<u>Term</u>	<u>Units</u>	<u>Description</u>
Q1	ml/min	Possible leakage into the system.
Q2	ml/min	Possible leakage out of the system, $Q1 = Q2$.
Sw	o/oo	Salinity in the overlying water.
DOw	mg/liter	Dissolved oxygen concentration in the overlying water.
Lw	mg/liter	Oxygen demand of the overlying water (BOD).
Sr	o/oo	Salinity in the respirometer.
DOr	mg/liter	Dissolved oxygen concentration in the respirometer.
DOr _i	mg/liter	Initial dissolved oxygen concentration in the respirometer.
Lr	mg/liter	Oxygen demand of the respirometer water (BOD).
Lr _i	mg/liter	Initial oxygen demand of the respirometer water.
Vr	liter	Volume of the respirometer.
K	l/min	Decay coefficient of the oxygen demand.
Sb	o/oo	Salinity of the bottom muds and interstitial water.
Lb	mg/liter	Oxygen demand of the interstitial water (BOD).
Lbr	mg/min	Rate of input of oxygen demanding material into the respirometer system from the covered mud area (A).
Ob	mg/min	Rate of oxygen diffusing into the covered bottom mud area (A).
A	m ²	Mud surface area covered by the respirometer.

Figure 11. - Explanation of Terms used in Benthic Respirometer Model.

Salinity Balance:

$$\frac{d(Sr)}{dt} = \frac{(Q)(Sw)}{Vr} - \frac{(Q)(Sr)}{Vr} \quad (3)$$

It was assumed that the only mechanism of salinity change was by direct leakage into and out of the system and that the volume of the respirometer was constant and completely mixed. Q_1 and Q_2 were assumed to be equal to Q . Some initial changes in salinity might be caused by bottom scour, but such changes could not be evaluated with the available data. Salinity changes that might arise from diffusion of material into or out of the bottom deposit were also considered to be small compared to changes due to leakage; therefore, terms containing S_b do not appear in equation 3.

A similar approach was used to model the changes in oxygen demand (BOD) and dissolved oxygen. The following equations resulted.

Oxygen Demand (BOD) Balance:

$$\frac{d(Lr)}{dt} = \frac{(Q)(Lw)}{Vr} - \frac{(Q)(Lr)}{Vr} - (K)(Lr) + \frac{Lbr}{Vr} \quad (4)$$

Dissolved Oxygen Balance:

$$\frac{d(DOr)}{dt} = \frac{(Q)(DOW)}{Vr} - \frac{(Q)(DOr)}{Vr} - (K)(Lr) - \frac{Ob}{Vr} \quad (5)$$

It was assumed that the rate of input of oxygen demanding material into the respirometer (Lbr) was independent of changes in respirometer BOD (Lr). No measurements were made to determine the effect of the interstitial BOD (Lb). Planktonic respirometer studies indicated that Lw was negligible. The diffusion of oxygen into the bottom deposit (Ob) was assumed to be at a constant rate.

Calculation of Leakage.

The availability of the benthal respirometer model made possible the calculation of leakage rates for the respirometer system using only salinity data for water in the respirometer and outside of the respirometer. By multiple regression analysis, curves could be fitted to measured salinity data so that the $\frac{d(Sr)}{dt}$, Sw , and Sr could be

evaluated at any time. Respirometer volume was a constant value of 60.4 liters. Therefore, all necessary values in the salinity mass balance equation were known, and estimates of leakage rates that occurred could be calculated using equation 3.

DO Uptake Rate Calculations.

Equations 3 and 5 were solved using the Runge-Kutta method for finite difference solutions. Fourth order solutions were obtained. Curve fits were used to input required measured quantities such as (DOr), (DOW), (Sr), and (Sw). By solving the salinity equation 3 and the dissolved oxygen equation 5 simultaneously, total oxygen uptake could be calculated by assuming $(-K(Lr)-Ob/Vr)$ to be the unknown rate of benthal oxygen demand exerted within the respirometer. When the build up of BOD within the respirometer and the removal of BOD from the respirometer is small, the total benthal uptake exerted within the respirometer may be divided by the bottom area of the respirometer to obtain the benthal oxygen uptake. Neglect of BOD build-up and release will lead to underestimates of the benthal oxygen uptake. Studies indicated, however, that this underestimate was quite small and could be neglected for the reported runs. Corrections could then be made for respirometer leakage. Therefore, even respirometer runs with high leakage rates could be corrected to obtain estimates of the oxygen uptake rates. The assumption that the benthal uptake rate was not changed because of the leakage mechanism was made.

During most benthal respirometer runs, slightly more rapid rates of oxygen demand were measured in the first hour of the run than for any succeeding time period. Furthermore, small increases in salinity usually occurred inside the benthal respirometers at startup. Therefore, during benthal respirometer start-up, water in the respirometer was replaced by disconnecting the return flow pipe at the PVC union and allowing the pump to introduce fresh water into the respirometer. Even then, rapid initial oxygen uptake often occurred. Only DO measurements taken after the initial rapid uptake were utilized in calculating DO uptake rates.

DO Uptake Results.

Light and dark planktonic respirometers failed to show any measurable oxygen demand or production at either of sites 2 and 3. Large mats of phytoplankton often found at site 2 were not included within these runs. Large DO variations, often found in the areas in which these dense growths appeared, indicated that production of dissolved oxygen and respiration by these growths is significant.

Using the large dark respirometer, sufficient field data to calculate leakage and uptake rates were collected during four runs at the Parker Slough site and during seven runs at the Toledo test site during the first grant year. Figures 12 and 13 show the variations in depth, salinity, temperature and dissolved oxygen for two of these runs. The corrected DO change, computed as previously described, is shown by the solid line in these figures.

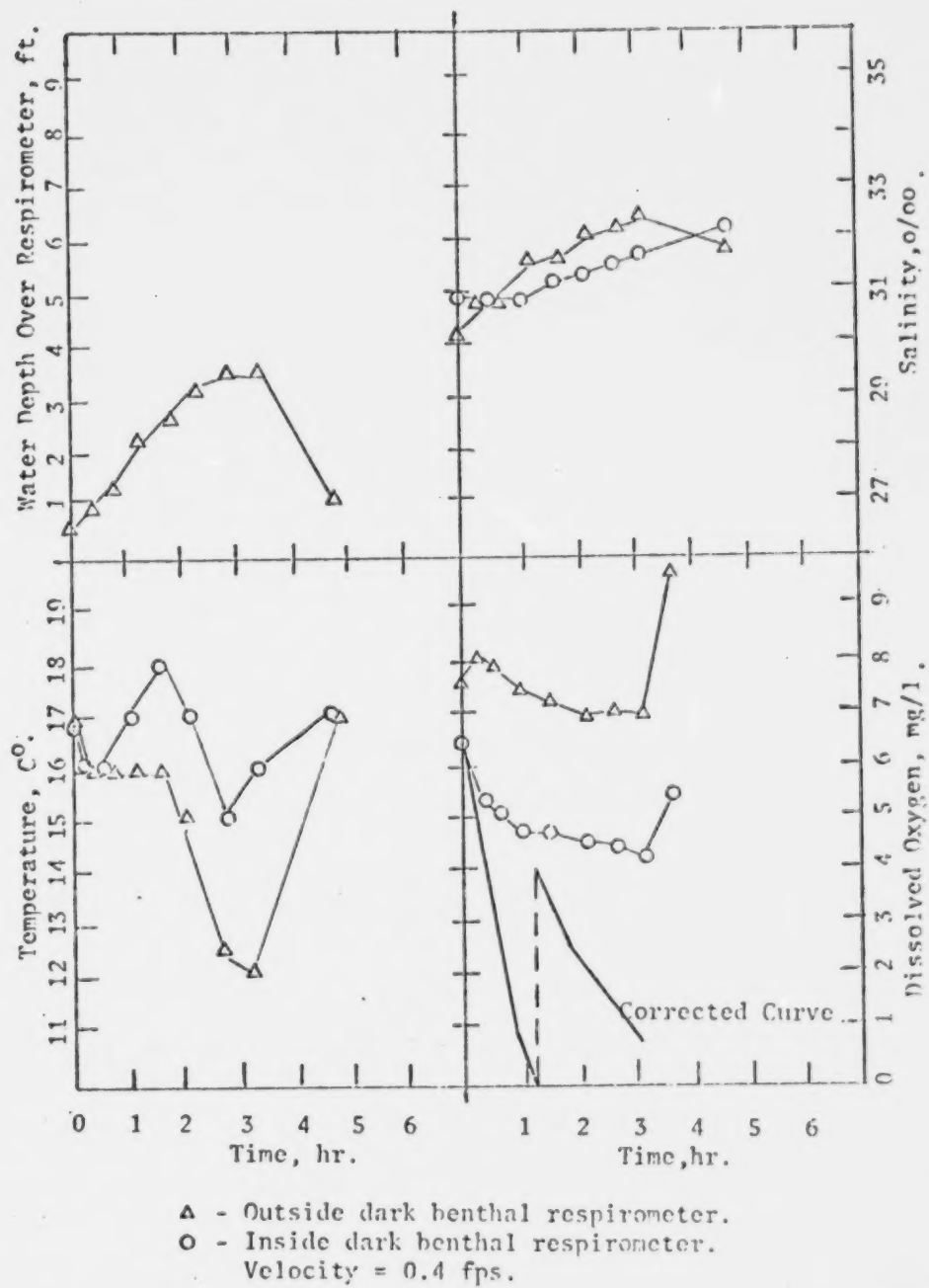


Figure 12. - Benthalthal Respirometer Data, Site 2, 9-11-69.

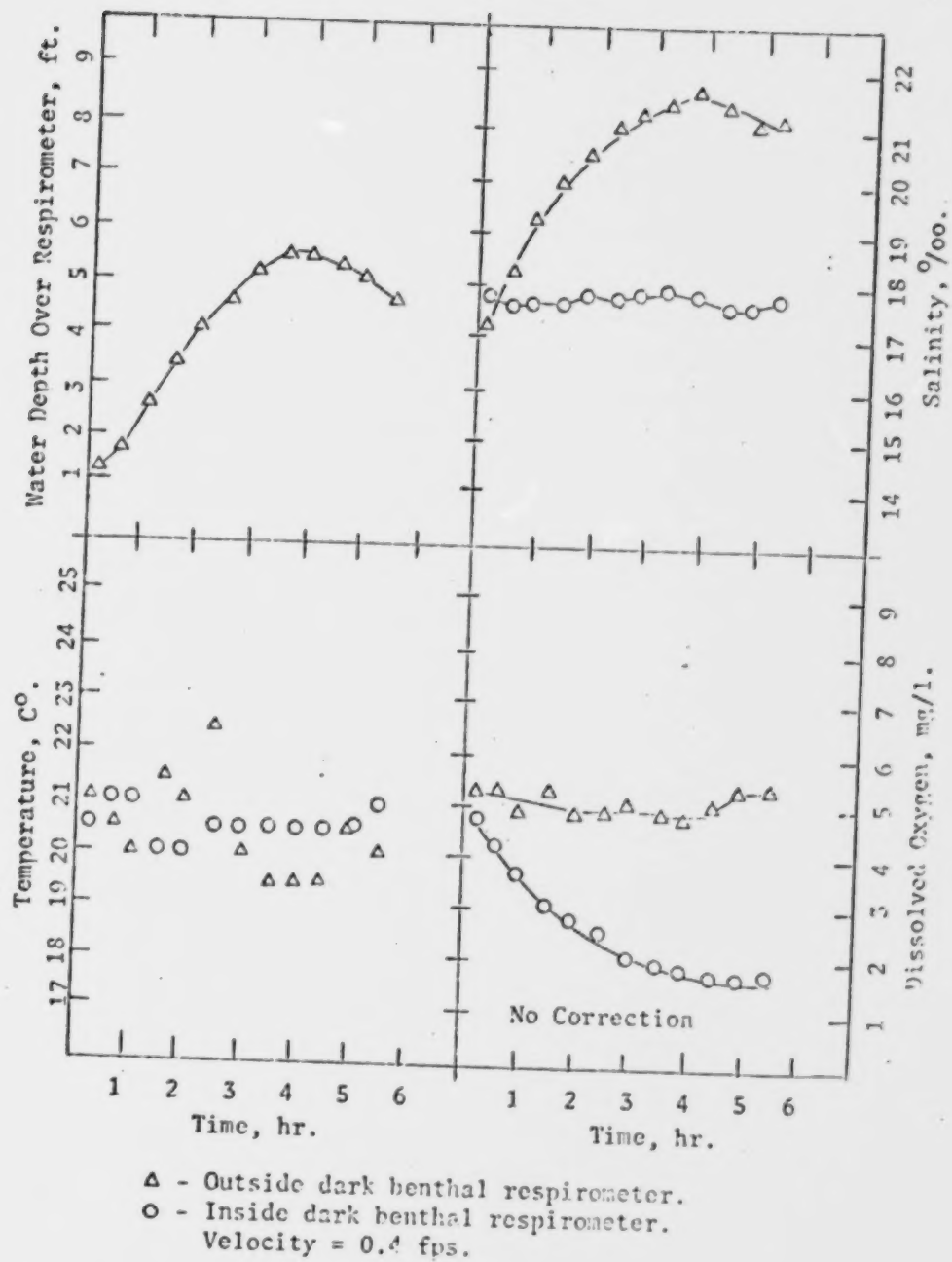


Figure 13. - Benthal Respirometer Data, Site 3, 9-8-69.

At site 3, benthic uptake rates averaged over each run ranged from 1.4 gm O_2/m^2 -day to 2.1 gm O_2/m^2 -day based on projected surface area.

In all runs, the DO uptake rate decreased with time as shown by the decreasing slope of the curves shown in figure 14. Leakage rates and actual DO concentrations within the respirometer also decreased with time. This resulted in apparent relationships between the uptake rate and the DO concentration and leakage rate as shown in figure 15. Whether these relationships are true or whether they merely reflect the simultaneous occurrence of unrelated variations is not apparent at this time. Oxygen uptake rates do appear however, to be related to the water velocity as indicated in figure 15A.

Table IV summarizes the average uptake values measured at site 3 for the various mixing velocities used. Table IV also shows the benthic uptake rates for the same muds measured in the laboratory studies. As can be seen, the in-lab mixed value is slightly higher than the values for benthic oxygen uptake measured during this research. Uncontrolled mixing, sample disturbance, differences in benthic plant respiration or a benthic deposit composition change might all account for these differences in uptake rates.

Excessive benthic respirometer leakage occurred at the site 2 test site as was seen by monitoring the salinity changes in the respirometer water. Leakage rates, calculated by use of the mathematical model, as high as 60 liters per hour were not uncommon. Extreme care during benthic respirometer placement did not result in a significant reduction of the leakage. Dye injections into an operating benthic respirometer at site 2 showed that the respirometer leaks were caused by the numerous mud shrimp burrows that penetrated the area. The mud shrimp burrows apparently formed an interconnecting maze of channels in the tidal flat deposit. On several occasions at low tide, surges of water were observed coming from shrimp holes located upshore from the low tidal water. The observed surges had the same period as small waves breaking against the exposed tidal flat. This further substantiated the inference that the shrimp burrows formed interconnecting networks and could form passages for water circulation.

Computer corrected benthic uptake rates of from 4.8 to 8.5 gm O_2/m^2 -day were calculated for site 2. Before correction for leakage rates, comparison of DO changes within the respirometers for the four runs

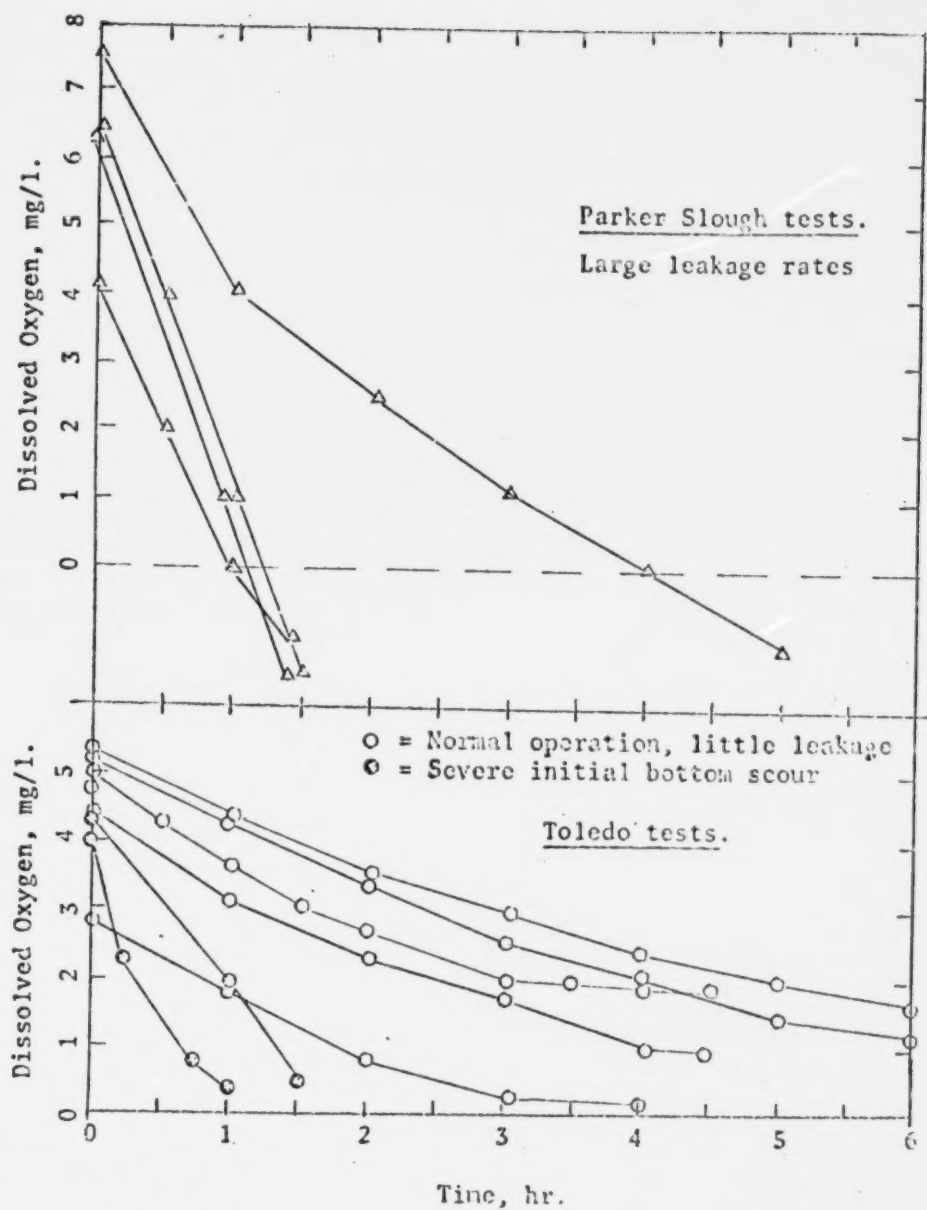


Figure 14. - Summary of Corrected Benthic Oxygen Uptake Rates at Sites 2 and 3.

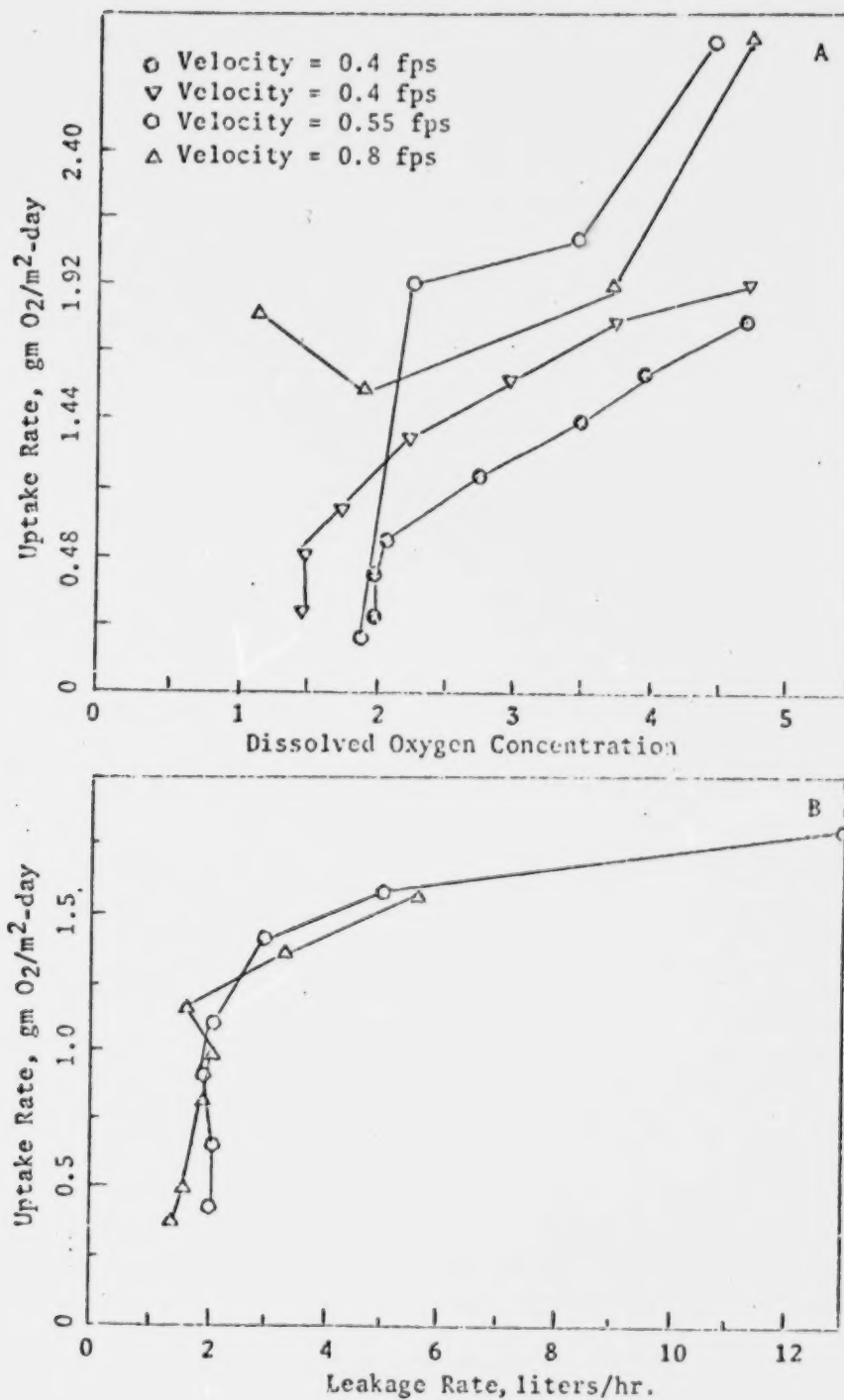


Figure 15. - Variation of Benthic Uptake Rates at Site 3.

TABLE IV
SUMMARY OF BENTHAL OXYGEN UPTAKE RATES AT SITE 3

<u>Method</u>	<u>Mixing Conditions</u>	<u>Uptake Rates^a gm O₂/m²-day</u>
Large Dark Respirometer	Velocity = 0.4 fps	1.4
Large Dark Respirometer	Velocity = 0.55 fps	1.7
Large Dark Respirometer	Velocity = 0.8 fps	2.1
Laboratory	No mixing	1.9
Laboratory	Plunger mix	3.5

^a based on projected deposit surface area.

at the Parker Slough site showed little similarity. The rates of DO change were significantly different and increases in the respirometer DO were occasionally measured. After correcting for leakage, the corrected DO changes showed a definite pattern. Three of the runs displayed quite similar uptake rates (see figure 14) while the fourth run displayed a lower uptake rate. The leakage rates for this fourth run were quite high and not reliable due to the small measured salinity difference inside and outside of the respirometer. The most reliable results, therefore, indicate that the Parker Slough area displayed an oxygen uptake rate approximately 4 to 6 times greater than that of the Toledo area, or about 8 gm/m²-day.

Simultaneous measurements using both the dark and light smaller respirometers indicated that the total benthic oxygen uptake depends to a large extent on the respiration of benthic plants. In regions of relatively high benthic photosynthetic oxygenation, as determined by a transparent benthic respirometer, uptake rates of 3 to 6 gms/m²-day were measured at site 1. At this same site, a lower rate of 1.4 gms/m²-day was measured in a region of low benthic photosynthesis. These results, in which the smaller respirometers were used are probably not as reliable as results obtained through the use of the larger respirometer.

The larger uptake rates measured at site 2 compared to site 3 (both measured by the large respirometer as previously discussed) appear to be due to the large number of shrimp burrows at site 2 and the larger amount of benthic plant respiration. Though no light respirometer runs were conducted at site 2, the extent of benthic photosynthesis was evident by measured DO concentrations as high as 25 mg/l. Also, the bottom at site 2 was observed to be covered with fine bubbles (presumably oxygen) on several occasions. Several respirometer runs had to be rejected because of the release of DO in the form of bubbles within the respirometer. Collection of the gas was attempted with limited success. Therefore, only those respirometer runs in which the DO was sufficiently below saturation to prevent bubble formation were utilized.

A single small dark respirometer run at site 4 measured an uptake rate of approximately 4 gms/m²-day. A study of DO variations within the overlying water indicated, however, that rates as high as 12 gms/m²-day could be expected.

Both laboratory and field studies indicated that the DO uptake rate was reduced by 30 to 40 percent when the system was poisoned with mercuric chloride. These experiments, however, were quite limited.

Sensitivity Study.

To further understand the mechanisms that control benthic oxygen uptake, sensitivity studies were made using the mathematical model previously described. Numerical approximations to the solutions of these equations were obtained by fourth order Runge-Kutta methods. By varying parameters in the dissolved oxygen equation and the BOD equation, curves of oxygen uptake similar to those measured were developed. It was found that, with the equations previously proposed, simulated DO variations corresponded to actual measured DO variations only if a major portion of the oxygen demand was due to one of the following:

- A. the transport of oxygen from the water into the deposits,
- B. demanding material released from the deposit into the water or
- C. combination of A and B from above.

First order decay coefficients, K , needed in assumption B were 10 to 100 times greater than those normally encountered for BOD tests of polluted waters. These results suggest that, under normal water flow conditions, the principal oxygen uptake due to tidal flat deposits occurs in the immediate vicinity of the deposits. Sulfides released from the anaerobic regions would result in such an uptake.

It should be recognized, however, that respirometer studies of approximately six hours may be too short to accurately measure the long term release of BOD. High BOD values in tidal flat waters were not found, indicating that such a mechanism was probably not substantial. Accurate measurements of BOD (possibly COD) throughout a respirometer run might lead to better estimates of such release. In general, it was found, however, that the BOD values were too low for sufficient accuracy.

SIMPLIFIED FREE SULFIDE MODELS

Model of Sulfide Transfer Through Aerobic Zone of Mud.

Consider a vertical column of deposit of cross sectional area A . Dissolved oxygen diffuses downward from the surface, while oxygen demanding substances diffuse upward. A second order reaction between the DO and these substances is assumed. The depth of the deposit, z , is taken as zero at the surface with positive values increasing with depth.

The rate change of DO mass within a horizontal slice from the vertical column having depth dz equals the sum of all DO import and removal rates for that slice. That is

$$\frac{\partial (AOn)}{\partial t} dz = F_i - F_o + G \quad (6)$$

in which n is volume of interstitial water within the slice divided by the total volume of the slice, F_i is the DO flux into the slice, F_o is DO flux out of the slice, O is the DO concentration and G is the sum of all DO sources and sinks within the slice. Taking

$$F_o = F_i + \frac{\partial F}{\partial z} dz \quad (7)$$

and substituting into equation 6 leads to

$$\frac{\partial (AOn)}{\partial t} dz = - \frac{\partial F}{\partial z} dz + G \quad (8)$$

The DO flux due to diffusion and dispersion (second term below) and water flow (third term below) is given by

$$F = - D_o A m \frac{\partial O}{\partial z} + A q O \quad (9)$$

in which m is the fraction of the surface area open to diffusion, q is the water transport rate per unit area, and D_o is the effective diffusion coefficient for DO. Included in the term D_o is the mixing due to molecular diffusion (due to flow through a porous media), burrowing organisms, wave action and other factors which result in vertical mixing.

The source-sink term of DO within the deposit will be taken as

$$G = \mu O C A n dz \quad (10)$$

in which μ is the second order reaction rate and C is the concentration of the oxygen demanding materials in solution which diffuse upward.

Oxygen demanding materials which have very low diffusion rates can be assumed to have been depleted from the aerobic zone of the deposit and thus are not included in C . Materials which are oxidized

slowly will not be included in C as they may be assumed to diffuse out of the deposit before exerting a substantial oxygen demand. The remainder of materials which do diffuse and are oxidized at relatively rapid rates are included in C. In tidal flat regions, the major component of C will likely be free sulfides.

All materials included in C will, for the present, be characterized by the same effective diffusion coefficient and the same second order reaction as shown in equation 10. This limitation of the model can be largely removed by dividing C into as many components as is deemed necessary.

Certain materials included in C become sorbed within the deposit. In the following work, only near steady state results will be utilized and thus an equilibrium between sorbed and non sorbed material can be assumed. The model does, however, give transient conditions and can be expanded to include sorbed and non sorbed materials if necessary.

Combining equations 8, 9, and 10 and taking A, n, D_o , m and q constant with distance and A and n constant with time leads to

$$\frac{\partial O}{\partial T} = \frac{D_o m}{n} \frac{\partial^2 O}{\partial z^2} - \frac{q}{n} \frac{\partial O}{\partial z} - \mu OC \quad (11)$$

As an approximation, both m and n may be taken as equal to the porosity. In the following discussion, convection will be taken as zero. Thus equation 11 reduces to

$$\frac{\partial O}{\partial T} = D_o \frac{\partial^2 O}{\partial z^2} - \mu OC \quad (12)$$

Similarly, for the oxygen demanding substances, one obtains

$$\frac{\partial C}{\partial T} = D_c \frac{\partial^2 C}{\partial z^2} - \mu OC \quad (13)$$

in which D_c is the effective diffusion coefficient for C.

The benthal oxygen uptake, OD' , due to materials included in C, is equal to the sum of the DO flux into the deposit and the flux of C out of the deposit. Thus

$$OD' = \left(D_o m \frac{\partial O}{\partial z} \right)_{z=0} - \left(D_c m \frac{\partial C}{\partial z} \right)_{z=0} \quad (14)$$

Respiration of benthal algae, which may be significant, and oxygen demand of materials which are released from the deposit but not included within C, both will contribute to the benthal oxygen uptake rate but are not included within OD'.

Approximations to the solutions of equations 12, 13 and 14 were obtained by explicit finite difference methods (64). Results shown in figures 16 and 17 were satisfactorily checked by comparison of identical finite difference runs utilizing different space and time intervals. Several runs were also satisfactorily compared with an implicit finite difference scheme.

At the surface (upper) boundary a DO concentration of 8.0 mg/l and a zero value of C were assumed unless otherwise noted. At the lower boundary, a constant value of C for each run and a DO concentration of zero were assumed. In all runs, the lower boundary was taken at a depth sufficiently great so that removal of DO above that depth was obtained. The position of the lower boundary and the value of C at this boundary were adjusted for any given run so as to result in the desired value of OD'. A value of 5.0 per mg/l-day was utilized for μ unless otherwise noted.

In figures 16 and 17 uptake rates, reported as OD'/m, were taken as 1.65-1.70 gm/m²-day unless otherwise noted. As the value of m can be expected to be approximately 0.4 (a porosity of 0.38-0.44 was determined at site 1), and as OD' can be expected to be approximately one half of the benthal oxygen uptake (substances not included in C compose the other half), the reported values of OD'/m can be interpreted as gross estimates of the total oxygen uptake exclusive of benthal plant respiration. Unless noted, D_O and D_C were set equal, the magnitude hereafter designated as D.

The relationship between the free sulfide concentration, S, and C will depend on: (a) the mass of free sulfides oxidized per mass of DO utilized and (b) the fraction of C due to free sulfides. As an approximation S may be taken as 50% to 100% of C.

Let

$$P_w = \frac{D_c m \frac{\partial C}{\partial z}}{OD'} \quad z=0 \quad (15)$$

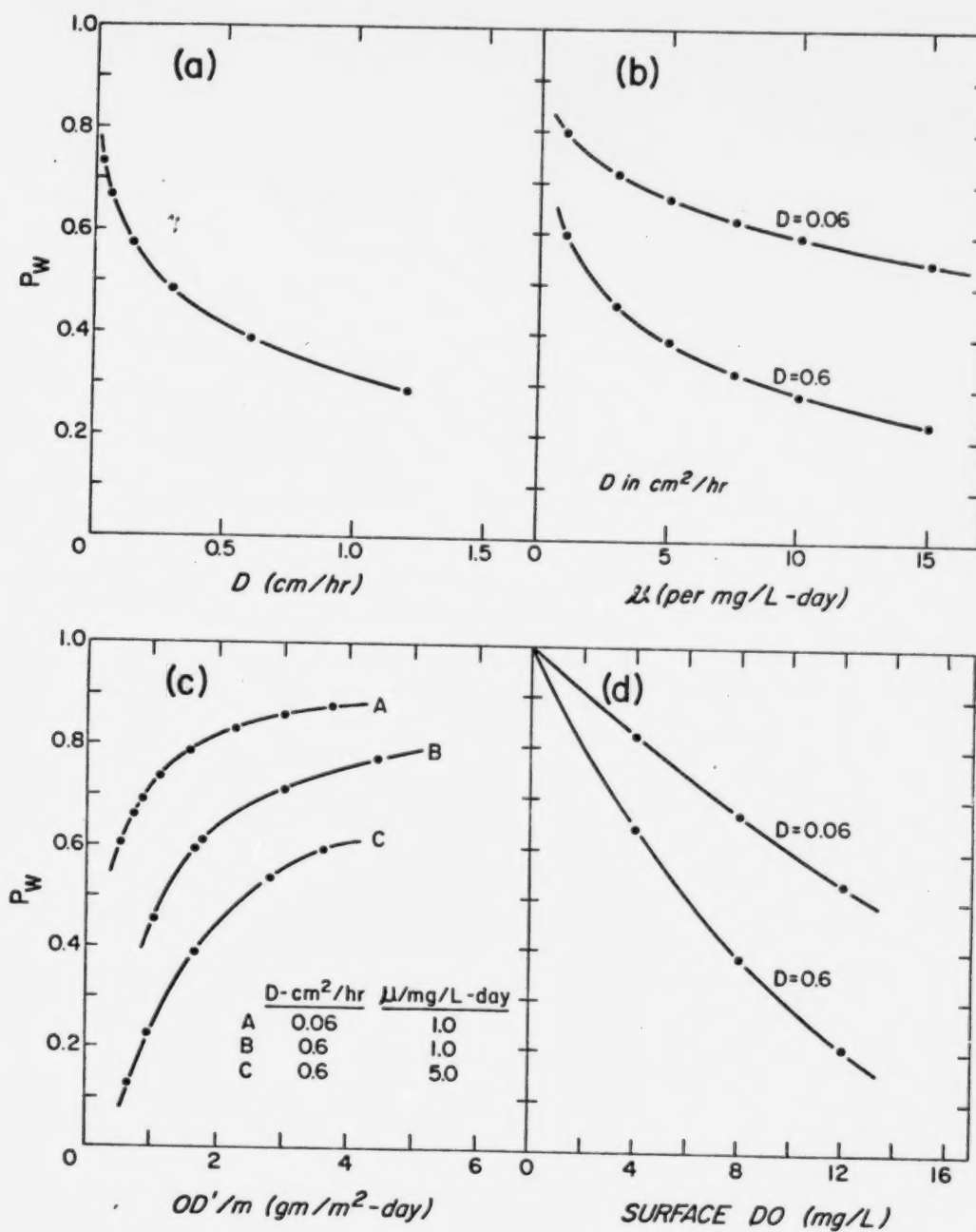


Figure 16 - Fraction of Bottom Oxygen Demand Exerted Within Overlying Waters Determined From Equations 6 and 7.

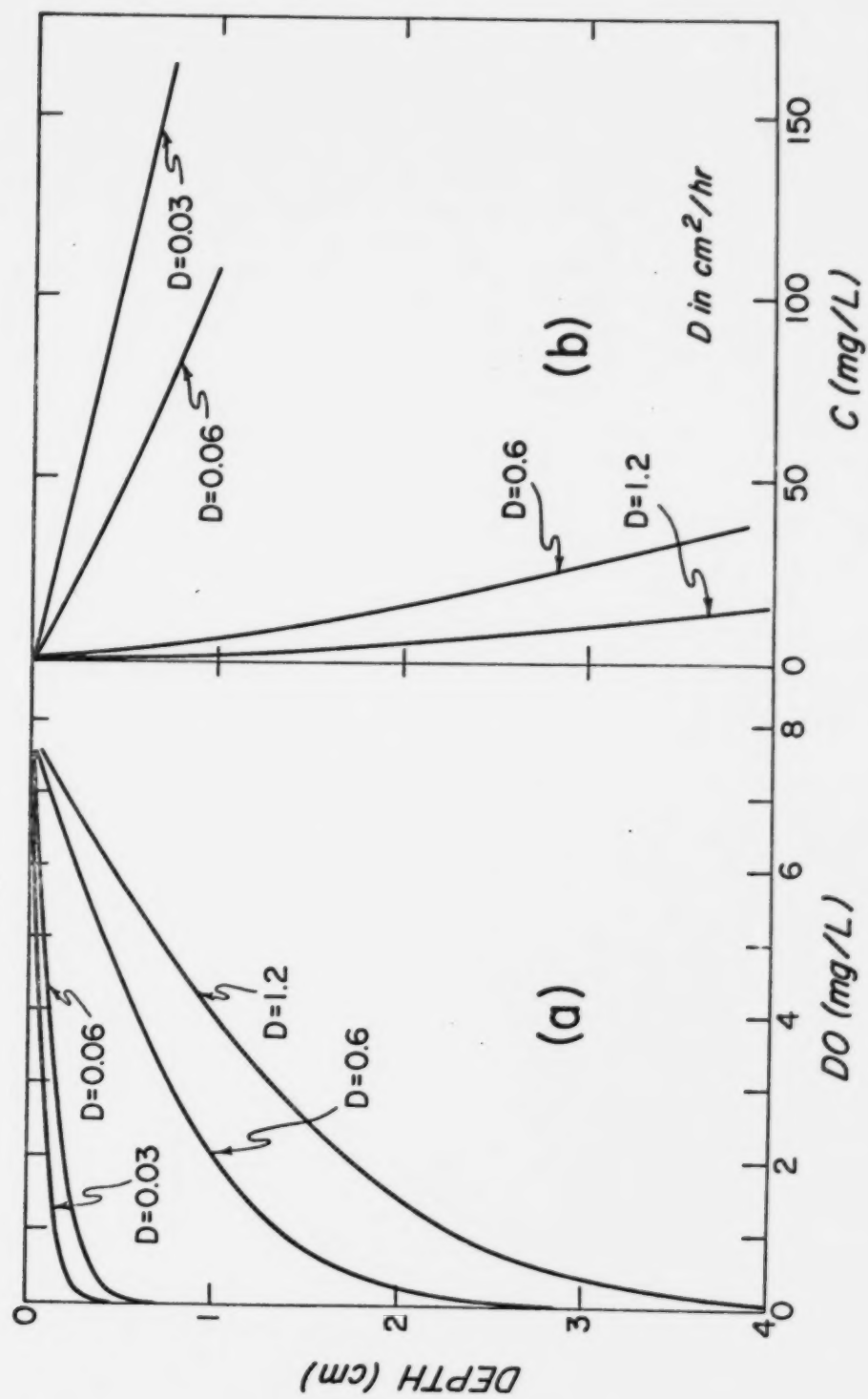


Figure 17 - Calculated Profiles of DO and Oxygen Demanding Materials.

in which P_w is the fraction of OD' due to the release of C to the overlying water. The results given in figure 16, show that P_w will be highest at low values of D and μ . Thus, the assumption that diffusing materials which are slowly oxidized will exert their oxygen demand within the overlying water rather than within the aerobic zone of the deposit appears to be warranted. When diffusion coefficients are of the magnitude of molecular diffusion (approximately $0.06 \text{ cm}^2/\text{hr}$), approximately 60 to 80 percent of OD' is due to the release of C from the deposit. At higher values of D , however, this percentage is reduced by approximately one half. Values of P_w decreased as D_c/D_o decreased.

The results shown in figure 16C indicate that P_w increases as the benthic oxygen uptake increases. This results from a reduction of the aerobic zone of the deposit and thus reduces the region of the deposit in which C may be oxidized.

The results shown in figure 16D demonstrate that P_w rapidly increases as the DO in the overlying water decreases.

Profiles of DO and C within the deposit are shown in figure 17. Values of OD' were nearly identical for all of the runs shown in figure 17. At values of D corresponding to molecular diffusion, the aerobic zone is reduced to several mm or less. This depth is increased to several cm as D is increased. Substantial reductions of C in the surface regions of the deposits resulted from increases of D .

Based on the results shown in figure 17, it is of interest to speculate on the effect of a pollutant which eliminated the macroorganisms which were mixing the upper portions of the deposits. The resulting reduction of D would lead to decreased DO levels and substantial increases of C within the upper regions of the deposit. The reestablishment of the macroorganisms after the removal of the pollutant might then be prevented by the low DO values and the toxicity of C (particularly the free sulfides). Thus the effect of the pollutant might indirectly persist long after the pollutant had been removed. An occasional pollutant might then have nearly the same effect as a continual pollutant.

Model of Free Sulfides in Overlying Water.

The following model will relate the free sulfide concentration in the overlying waters to several more commonly known parameters. It is intended that the model will only estimate the order of magnitude of free sulfide concentrations. A more fundamental model, which includes processes illustrated in figure 1, is not now presented but will be included in a later section of this report.

Consider a vertically mixed column of water of depth H and horizontal area A. A deposit at the bottom of the column has a total oxygen uptake rate given by OD. The upper surface of the water column is exposed to the air. The fraction of OD due to free sulfides formed within the anaerobic regions is P_S .

Performing a mass balance on the sulfides within the water column leads to

$$\frac{d(AHS)}{dT} = YAP_w P_S OD - AHR_S - AM \quad (16)$$

in which R_S is the oxidation rate per unit volume of S within the water, Y is the mass of S oxidized per mass of DO utilized, and M is the transfer rate of sulfides per unit area through the air water interface. It is assumed that transport of fresh water into the column is negligible.

Take

$$R_S = KS \quad (17)$$

in which K is the reaction coefficient of S oxidation at a given DO concentration. Assuming a second order reaction leads to

$$K = \mu C \quad (18)$$

The sulfide loss to the atmosphere will be taken as

$$M = K_A fS \quad (19)$$

in which f is the fraction of the free sulfides present as H_2S and K_A is the transfer coefficient of H_2S across the air-water interface.

Equations 16, 17 and 18 may be combined to form

$$\frac{d(AHS)}{dT} = AYP_w P_S OD - AHKS - AK_A fS \quad (20)$$

By assuming a steady state, equation 20 reduces to

$$S = \frac{YP_w P_S OD}{HK + K_A f} \quad (21)$$

Large differences between observed and computed concentrations from equation 21 should be expected. The assumptions of no fresh water input, steady state and complete vertical mixing in particular contribute to the limitations of equation 21. When judiciously applied, equation 21 can be used, however, to estimate the general magnitude of free sulfide concentrations in overlying waters during periods of relative stability.

An examination of the four sample sites indicate that the conditions at site 4 were most favorable for the presence of high free sulfides within the overlying waters. Small particle size, low water flow, low mixing within the deposits, low night DO concentration, poor drainage, available sulfates from the sea water, and high organics all could be expected to contribute to high free sulfide concentration.

Estimates of parameters in equation 21 which might apply to conditions found at site 4 are listed in Table V. It is emphasized that these values are estimates based on a variety of experimental conditions and that they should not be considered as absolute.

The range of free sulfides concentration, S , in the overlying water computed by equation 21 using the parameters shown in Table V is enclosed by the solid lines of figure 18. These results illustrate that high free sulfide concentrations in the overlying water may occur under conditions similar to those found at site 4.

The value of K_A given in Table V is relatively low and would be expected to occur during periods of relative calm. Under these conditions oxygen transfer across the air-water interface would also be low. If the benthic oxygen uptake was relatively high and photosynthetic oxygenation was low or absent (night conditions), the DO would be expected to fall to near zero values. Under such conditions, P_{SOD} would remain nearly constant (though OD would likely decrease), K would become small and P_W would approach unity. The free sulfide concentration might then increase to levels higher than the ranges indicated in figure 18 with concentrations largely controlled by the release of H_2S to the atmosphere.

FREE SULFIDES IN OVERLYING WATER

Methods.

During the late summer-early fall of 1970, water directly above the sediment of the four sites was monitored during a tidal cycle for dissolved free sulfides and dissolved oxygen. Profiles of DO and free sulfides above the bottom were determined by simultaneously drawing

Table V. - Estimates of Parameters from Equation 21
Applicable to Site 4.

Parameter	Range	Reference
Y	1.0	(34)
P _w	0.8	This work
P _s	0.3-0.4	(11) (55)
OD	4.0-12.0 (gms/m ² -day)	a
K	8.0-70.0 (per day)	(28) (33) (37) b
K _A	0.5 (meters/day)	(67) (46) c
f	0.4-0.5	d

a - estimated from field studies

b - obtained in sea and brackish water

c - reference (67) shows similarity between DO and H₂S transfer; reference (46) gives DO transfers for low wind velocities.²

d - based on pH of approximately 7 at site 4

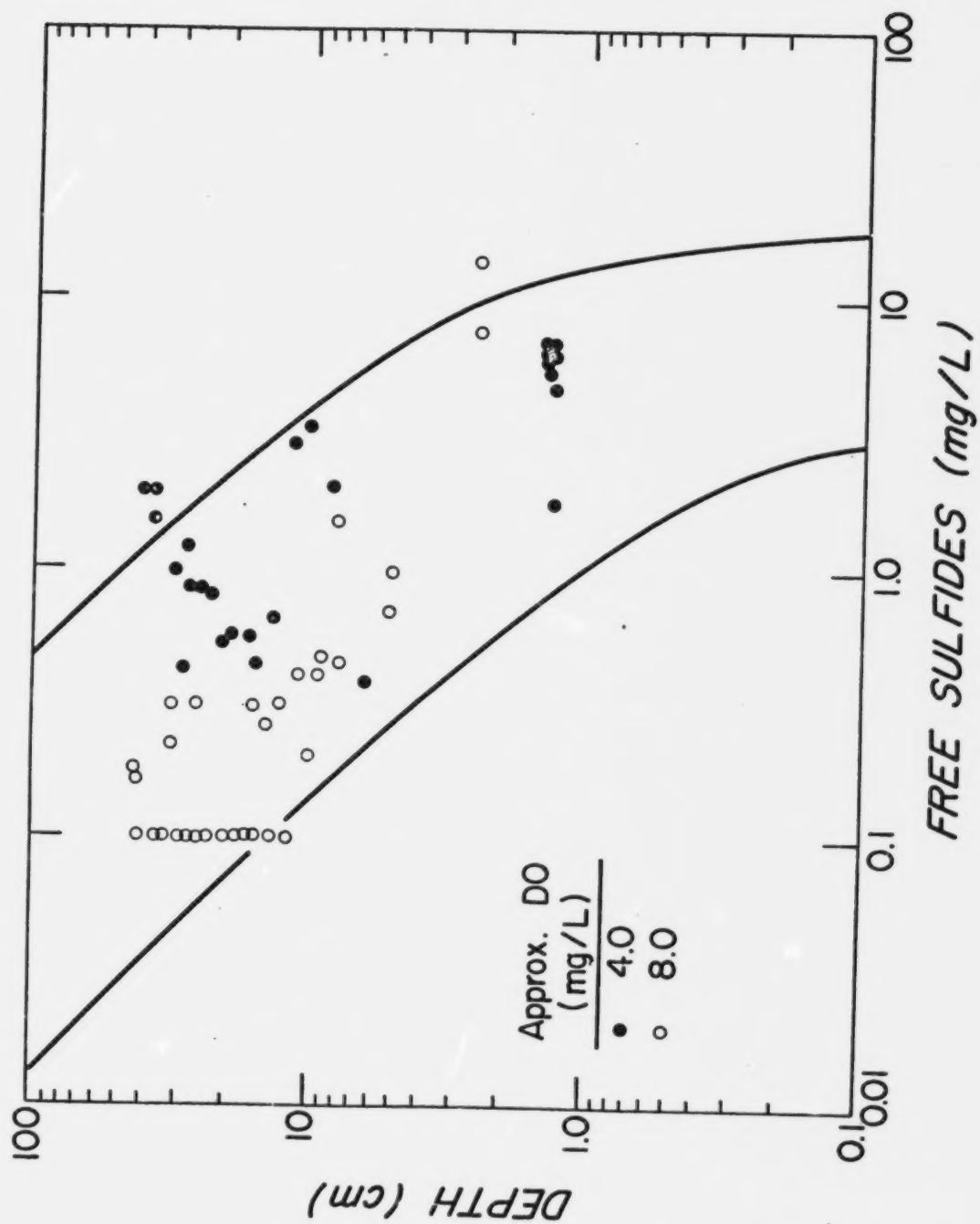


Figure 18 - Range of Free Sulfides in Overlying Water.

water into six 50 cc plastic syringes attached by small bore tygon tubing to six 1.5 mm ID stainless tubes set horizontally at varying heights above the deposit. DO was determined on 20 ml. water samples collected in 30 cc plastic syringes by a 'micro-winkler' method (54). Free sulfides were determined by immediately fixing 20 ml of water sample inside the syringe with an equal volume of 50% antioxidant buffer solution. The standard solution, containing 320 gm sodium salicylate, 72 gm ascorbic acid, 80 gm sodium hydroxide and made up to one liter in distilled water, prevents further oxidation of sulfide and fixes the free sulfides as essentially all free sulfide ions (65). Sulfide content was then determined by measuring potential on a pH meter equipped with a sulfide membrane electrode, and reading the sulfide concentrations from a standard curve developed prior to each run (66). This method was compared with results obtained titrimetrically with iodine (4) and titrimetrically with lead perchlorate using the probe as an end-point indicator (66). Results showed very close agreement among all three methods.

Discussion.

Free sulfide and DO profiles measured during daylight conditions at site 4 are shown in figure 19. Due to the benthal photosynthetic oxygenation, DO values were highest near the mud-water interface. Significant free sulfide concentrations were measured despite the relatively high DO values. Higher free sulfide concentrations were measured in the low mixed water region immediately adjacent to the mud-water interface.

Results from four sampling periods are shown in figure 20. A drop in the DO is noted in figures 20b and 20c due to the nighttime cessation of photosynthetic oxygenation. The lower DO values lead to higher free sulfide concentrations.

After an initial drop in DO, the free sulfide and DO concentrations shown in figures 20b and 20d become relatively stabilized with DO concentrations remaining at approximately 4 mg/l and 8 mg/l respectively for approximately three hours. The free sulfide concentrations measured during these relatively stable periods are plotted with approximate water depths (the bottom had an unevenness of several centimeters) on figure 20. These free sulfide concentrations generally fall within the range estimated by equation 21 with the upper range being more closely approached for the lower DO (4 mg/l) conditions and the lower range being more closely approached for the higher DO (8 mg/l) conditions.

No similar stability is found for the results shown in figure 20c. Free sulfide concentrations varied considerably, with highest concentrations occurring when DO concentrations were lowest.

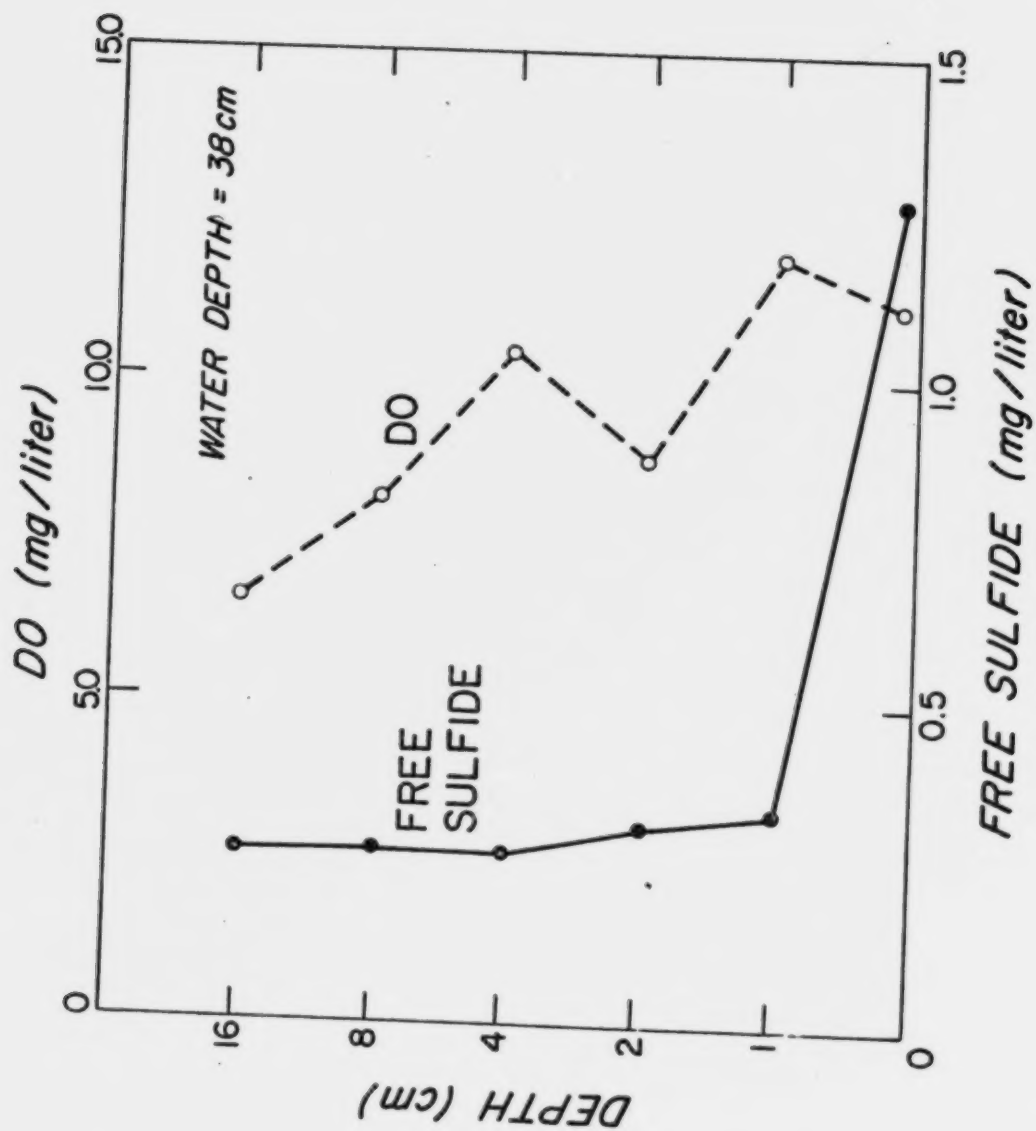


Figure 19 - DO and Free Sulfide Profiles at Site 4.

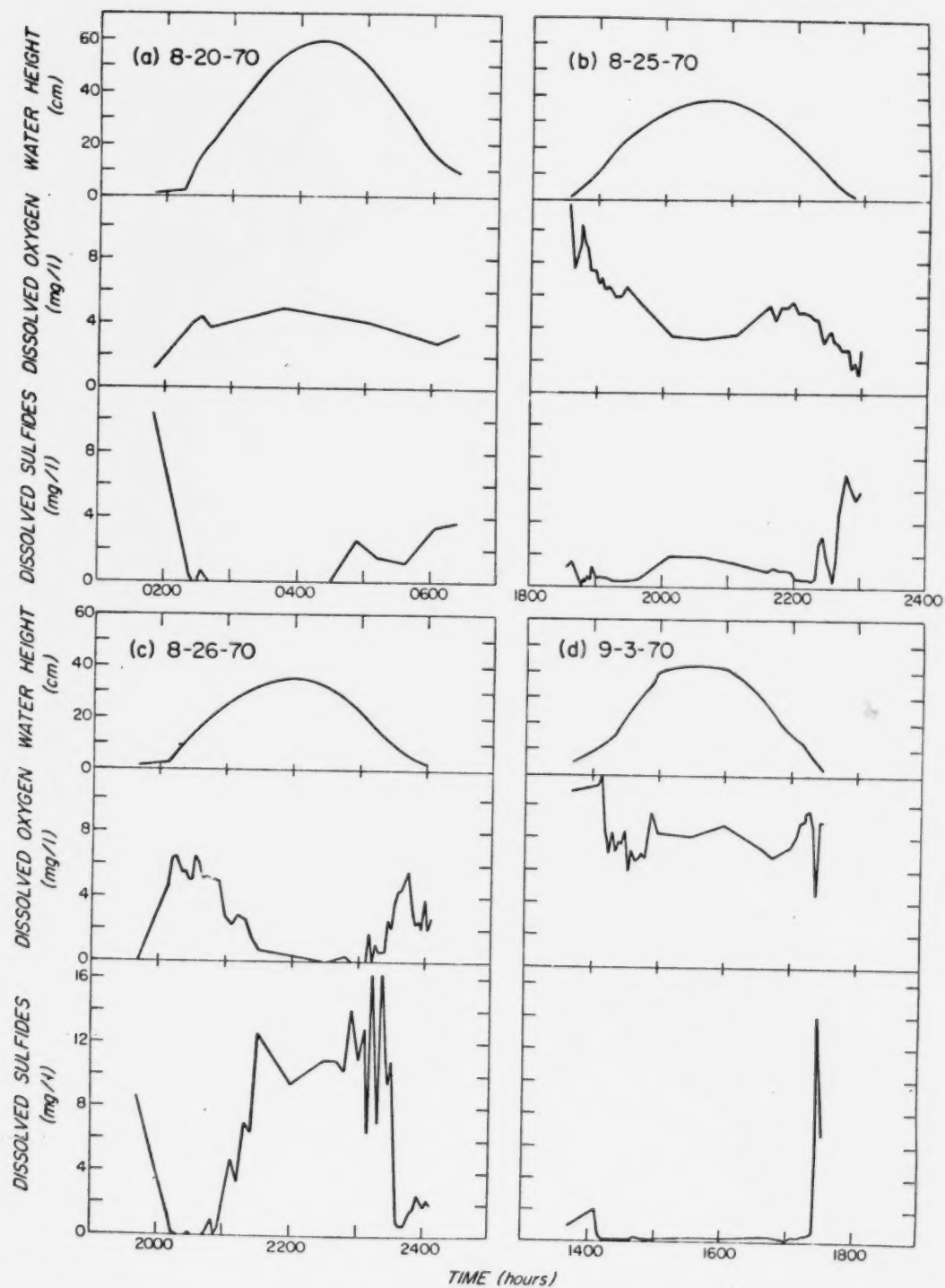


Figure 20 - Variation of DO and Free Sulfides Within Overlying Waters of Site 4.

The daytime results (figure 20d) also display significant free sulfide concentrations, particularly during periods of shallow water depth.

Most of the results from site 4 show a sudden increase in the free sulfide concentration at shallow water depths during the ebbing tide. Drainage from higher regions and drainage of some interstitial water may have contributed to this increase.

No detectable free sulfides were measured within the overlying waters of site 1 during the late summer-early fall sampling period. The lower oxygen uptake rates, larger particle size, greater hydraulic flushing, lower organic content and relatively high DO concentration (seldom below 6 mg/l) found at site 1 are all conditions which lead to low free sulfide concentrations.

At site 3, fine silt and clay particles within the deposits and a higher organic content (wood chips from a nearby pulp mill and saw mill were quite prevalent) provide conditions favorable toward the benthal release of free sulfides. Water velocities in at this site, however, were relatively high and the slope of the deposits prevented pools from forming during low tide. During the period of study, DO concentrations seldom fell below 5 mg/l. Total sulfides and organics within the interstitial sediment waters were relatively high at site 3 (see Table III). The high volatile solids were due, in part, to the large amount of wood chips found at site 3. The continued presence of free sulfides within the overlying waters was not measured at site 3, however, periodic concentrations of approximately 1 to 2 mg/l were measured during periods of slight surface scour. Free sulfides were noticeable during the ebbing of the tide at shallow depths when wave action appeared to disturb the mud surface. Site 3 was thus characterized by a periodic release, rather than a continued release, of free sulfides.

Sulfide profiles, similar to figure 19, though lower in concentration, have been measured in a fresh water system (38).

Note: this section has been substantially revised

GENERAL BENTHAL DEPOSIT MODEL

General.

In this section, a model is developed which more closely describes the processes illustrated in figure 1, than did the previous model. Several principal assumptions used in the model are listed below.

1. The model will be one-dimensional; considering only variations in the vertical direction.
2. The model will assume an equilibrium between sorbed and non sorbed materials.
3. The model will assume an initial distribution of organics and no addition of total organics will be included. The addition of organics through settling, primary production and other sources will later be included as an expansion of the model.
4. It will be assumed that the biological reactions are not limited by the concentrations of the microorganisms.
5. As in all models, many different substances will be grouped into large categories. As an example, soluble organics will be grouped into two categories (degradable and nondegradable). If necessary, these groupings may be broken down further.
6. Several additional assumptions, such as an identical inhibition of all anaerobic reactions by dissolved oxygen can be observed by inspection of the model.

General Notation.

The following general notation will be utilized.

1. G preceding a second symbol will signify a rate change per unit volume of water. The second symbol, following the G, will define the substance changing.
2. R will signify a maximum rate assuming no limiting materials and no inhibition. Subscripts on R will define the particular reaction.
3. The star superscript (*) will signify a coefficient pertaining to an aerobic reaction.

New specific notation will be defined as the model is developed. Organics will be expressed by the chemical oxygen demand (COD).

General Description of Soluble Materials.

Consider a vertical section of deposit and overlying water of horizontal cross sectional area A. Positive depth z, is measured from the water surface downward. Taking a mass balance on a slice of depth dz within the deposit leads to

$$\frac{\partial (AndzS')}{\partial t} = F_i - F_o + n(GS')Adz \quad (22)$$

in which n is the fraction of the deposit filled with water, S' is the concentration of a soluble substance, F_i is the total flux of this substance into the slice, F_o is the flux of the substance out of the slice and (GS') is the sum of the addition and removal rates per unit volume of water of S' within the slice.

The flux is S' due to convection and dispersion is taken as

$$F = -D_s, Am \frac{\partial S'}{\partial z} + UAmS' \quad (23)$$

in which D_s, is the vertical dispersion coefficient for S', U is the vertical velocity (positive downward) and m is the fraction of A open to diffusion and convection. Let

$$F_o = F_i + \frac{\partial F}{\partial z} dz \quad (24)$$

Substituting equations (23) and (24) into equation (22) leads to

$$\frac{\partial (AnS')}{\partial t} = \frac{\partial (D_s, Am \partial S' / \partial z)}{\partial z} - \frac{\partial (UAmS')}{\partial x} + n (GS')A \quad (25)$$

Assuming A to be constant with distance and time and n to be constant with time reduces equation (25) to

$$\frac{\partial S'}{\partial t} = \frac{1}{n} \frac{\partial (D_s, m (\partial S' / \partial z))}{\partial z} - \frac{\partial (UmS')}{\partial x} + (GS') \quad (26)$$

which is taken as the general equation for a soluble material within the vertical slice. Equation (25) can be used within both the deposit and the overlying water. In the overlying water n and m will equal

unity, while both will have lower value (approximately 0.4) within the deposit. In addition, D_S' will be substantially greater within the overlying water.

General Equation for Insoluble Materials.

For the present, no insoluble materials will be included in the overlying water. Thus, following a similar mass balance as above, one obtains the general equation for insoluble materials shown below

$$\frac{\partial I'}{\partial T} = (GI') \quad (27)$$

in which I' is the concentration of the insoluble materials and (GI') is the sum of the sources and sinks of insoluble materials at a particular depth.

Promoters and Inhibitors.

The primary differences between the various substances included in the mass balance will be expressed in the terms (GS') and (GI') . Difference in D_S' may also be expected particularly when dispersion is reduced to molecular diffusion.

Reaction rates which determine (GS') and (GI') will be determined by the concentrations of two types of substances; substances which promote the reaction and substances which inhibit or retard the reaction.

As an example, DO would promote aerobic reactions and inhibit anaerobic reactions. Let P be the concentration of a substance which promotes the reaction while I is the concentration of a substance which inhibits or retards the reaction.

Considering a unit volume of water, reaction promotion will be expressed by the common Michaelis-Menten equation shown below

$$G = R \left(\frac{P}{K_p + P} \right) \quad (28)$$

in which G is a given reaction rate per unit volume of water, R is the maximum reaction rate and K_p is the concentration of P when G equals one half R , assuming no other promoters or inhibitors reduce the reaction rate. A star (*) superscript will denote K values applicable to aerobic reactions. When multiple promoters occur

equation (28) can be expanded to

$$G = R \left(\frac{P_1}{K_{P_2} + P_1} \right) \left(\frac{P_2}{K_{P_2} + P_2} \right) \left(\frac{P_n}{K_{P_n} + P_n} \right) \quad (29)$$

Promoters will generally be classified into substrates and hydrogen acceptors.

Inhibitors will be assumed to operate by two methods. First, they may restrict the utilization of a particular promoter. This is expressed by the equation

$$G = R \left(\frac{P_1}{K_{P_1} + \frac{P_1}{K_{I_1}} I_1 + P_1} \right) \left(\frac{P_2}{K_{P_2} + P_2} \right) \quad (30)$$

in which the utilization of P_1 is inhibited by I_1 . (P_2 is not affected) In equation (30), the effect of I_1 can be compensated by an increase in P_1 .

The second type of inhibition or restriction is given by the equation

$$G = R \left(\frac{P_1}{K_{P_1} + P_1} \right) \left(\frac{P_2}{K_{P_2} + P_2} \right) \left(1 - \frac{I_1}{F_{I_1} + I_1} \right) \left(1 - \frac{I_2}{F_{I_2} + I_2} \right) \quad (31)$$

in which F is the concentration of an inhibitor at which the reaction is reduced by one half. The sharpness of the inhibitor effect can be increased by raising I and F to higher powers.

In the following model, inhibitors will be included as shown in equation (31) in which the effect of inhibitors is independent of the concentration of promoters (unlike equation (30)).

Insoluble Organics.

The source and sink term for insoluble organics is given by

$$GIO = - (GIO)_1 - (GIO)_2$$

in which $(GIO)_1$ is the aerobic breakdown rate of insoluble organics and $(GIO)_2$ is the aerobic breakdown rate of insoluble organics.

The following equations will be applied.

$$\begin{aligned} (GIO)_1 &= R_{IO}^* \left(\frac{b \cdot IO}{K_{IO}^* + b \cdot IO} \right) \left(\frac{O}{K_O + O} \right) \left(1 - \frac{S}{F_S^* + S} \right) \\ (GIO)_2 &= R_{IO} \left(\frac{b \cdot IO}{K_{IO} + b \cdot IO} \right) \left(1 - \frac{O}{F_O + O} \right) \left(1 - \frac{S}{F_S + S} \right) \end{aligned} \quad (32)$$

in which O is the concentration of dissolved oxygen, S is the concentration of free sulfides, IO is the concentration of insoluble organics and b is the fraction of the COD that is biodegradable.

Soluble Organics.

The source and sink term for soluble organics is given by

$$\begin{aligned} (GSO) &= f(GIO)_1 + f^*(GIO)_2 \\ &- (GSO)_1 \\ &- (GSO)_2 \\ &- (GSO)_3 \end{aligned} \quad (33)$$

in which f is the fraction of the COD remaining after the conversion of insoluble to soluble, SO is the concentration of soluble organics, $(GSO)_1$ is the background rate of SO per unit volume of water due to aerobic decomposition, $(GSO)_2$ is the breakdown rate of SO due to sulfate reduction and $(GSO)_3$ is the breakdown rate of SO due to other anaerobic processes.

The following equations will be applied

$$\begin{aligned} (GSO)_1 &= R_{SO}^* \left(\frac{SO}{K_{SO}^* + SO} \right) \left(\frac{O}{K_O + O} \right) \left(1 - \frac{S}{F_S^* + S} \right) \\ (GSO)_2 &= R'_{SO} \left(\frac{SO}{K_{SO} + SO} \right) \left(\frac{SUL}{K_{SUL} + SUL} \right) \left(1 - \frac{O}{F_O + O} \right) \left(1 - \frac{S}{F'_S + S} \right) \end{aligned}$$

$$(GSO)_3 = R_{SO} \left(\frac{SO}{K_{SO} + SO} \right) \left(1 - \frac{O}{F_O + O} \right) \left(1 - \frac{S}{F_S + S} \right) \quad (34)$$

In which R'_{SO} denotes the maximum rate of SO removal per unit volume of water due to sulfate reduction while R_{SO} applies to all other anaerobic processes. SUL is the concentration of sulfates (SO_4) and F_S' describes the inhibition of S on sulfate reduction.

Sulfates.

The reaction of sulfates is given by

$$(GSUL) = - Y_{SUL} (GSO)_2 \quad (35)$$

in which Y_{SUL} is the mass of sulfate utilized per mass of COD oxidized by sulfate reduction. It is assumed that the source of SUL resulting from the biological and chemical oxidation of sulfides can be ignored when compared to the dispersion of SUL downward.

Sulfides.

Let

$$\begin{aligned} (GS) &= Y_S (GSO)_2 + Y'_S (GSO)_3 \\ &\quad (GS)_1 \\ &\quad - (GS)_2 \\ &\quad - (GS)_3 \end{aligned} \quad (36)$$

in which Y_S is the mass of sulfides released per mass of COD removed through sulfate reduction, Y'_S is the mass of sulfide released per mass of COD removed anaerobically (non sulfate reduction) resulting from the sulfur within the organic materials (putrification), $(GS)_1$ is the loss rate of sulfides (S) per unit volume of water due to the chemical reaction with DO, $(GS)_2$ is the removal rate of S due to the anaerobic photosynthetic sulfur bacteria and $(GS)_3$ is the removal rate of S due to the aerobic autotrophic bacteria.

The following equations will be applied

$$\begin{aligned}
 (GS)_1 &= \mu(O)(S) \\
 (GS)_2 &= R'_S \left(\frac{S}{K_S + S} \right) \left(\frac{L}{K_L + L} \right) \left(1 - \frac{O}{F_O + O} \right) \\
 (GS)_3 &= R^*_S \left(\frac{S}{K_S + S} \right) \left(\frac{O}{K_O + O} \right)
 \end{aligned} \tag{37}$$

in which μ is the second order coefficient for the chemical oxidation of S and L is the light intensity.

Dissolved Oxygen.

Let

$$\begin{aligned}
 (GO) &= -(1-f)(GIO)_1 \\
 &\quad - (GSO)_1 \\
 &\quad - Y_{OS}(GS)_1 \\
 &\quad - Y_{SO}(GS)_3
 \end{aligned} \tag{38}$$

in which Y_{OS} is the mass of O utilized per unit mass of S chemically oxidized, and Y_{SO} is the mass of O utilized per unit mass of S oxidized by aerobic sulfur bacteria. It is assumed that the COD loss in the anaerobic solubilization would result in an insignificant loss of O.

Combined Equations.

Equations (26) through (38) combine to form a model of an estuarine benthal system. All of these equations may be included both within the interstitial water and within the overlying water. (As previously stated, interstitial and overlying water differ principally by the values of D, n, and m.) The lower boundary will likely be relective, while the upper boundary condition at the water surface will be relective except for gases which transfer between the water and the atmosphere.

The model serves to quantitatively express concepts concerning the processes that occur within an estuarine benthal system. The limitations of the concepts of course are not removed when these

concepts are put in mathematical form. Thus, proper use of the model involves a continual evaluation of its limitations. The model, hopefully, will permit one to develop new concepts which arise by the interaction of the basic concepts from which the model was built. Sensitivity studies with the model will eventually serve to estimate which factors have the greatest influence on behavior of the benthal system. The model can thus indicate where experimental effort might most profitably be exerted. Ultimately, it is anticipated that the model will serve to describe (through probably not to a high degree of accuracy) the benthal response to a given environmental change, be it man-made or natural.

Finite-difference procedures will be used to obtain approximations to the solutions of equations (25) through (38). At the present date (Dec. 1970) the complete model has not been programmed, though portions of the model have. Programming of the model will be initiated during the remainder of the grant period, being completed by the first month of the next grant period. As a result of model, laboratory and field experiments, the model will likely change to some degree.

Currently, experiments are being initiated to better define the processes expressed within the model; particular attention is being devoted to reactions $(GIO)_2$, $(GSO)_1$, $(GSO)_2$, $(GSO)_3$, and $(GS)_1$.

CHAPTER 111

THE ESTUARINE SYSTEM

Introduction.

This chapter will be concerned with the estuarine system of which the tidal flats are important components.

Approach.

During the first grant year, a tidal study of the Yaquina, Alsea and Siletz was conducted. A water quantity-quality numerical model was also developed during the first grant period. The model is based on the one-dimensional equation given below.

$$\frac{\partial (AC)}{\partial T} = \frac{\partial (DLA \frac{\partial C}{\partial X})}{\partial X} - \frac{\partial (UAC)}{\partial X} - K_1 AC \quad (39)$$

In equation 39, A is the cross sectional area of the channel, D_L is the longitudinal dispersion coefficient, X is the longitudinal distance along the length of the estuary, T is time, K_1 is the first order decay coefficient and C is the material concentration. Finite-difference approximations to equation 39 were utilized. The mathematical model was then modified so as to include tidal flat areas and sloughs as separated identities adjacent to the main channel.

A series of model runs were conducted in which tidal variations were included. The Yaquina estuary served as the prototype, although a great deal of effort was not spent during this time to closely model the Yaquina. The results indicated that pollutant profiles within the estuaries were generally far more sensitive to variations in K_1 than to variations in D_L . These results suggested that a greater effort should be expended to better define the biochemical reactions, particularly within tidal flat areas, and a lesser effort should be given to the study of tidal hydraulics and dispersion.

The results of the expanded tidal flat study have been discussed in the previous chapter of this report. Field studies to investigate tidal hydraulics and dispersion were not conducted during the second

grant year. Mathematical model studies, however, were continued. Data obtained during the first grant year and data presented in the literature was reviewed and utilized.

Estuaries Involved in Study.

The term, estuary, is generally used to describe the lower reaches of rivers or coastal areas where fresh water and sea water interact under tidal influence. The type of estuaries studied under this project can be further classified as well mixed to partially stratified coastal plain estuaries (drowned river valleys). These estuaries have narrow entrances leading into a bay area followed by a channel of decreasing cross sectional area.

Yaquina Bay contains approximately 2,853 acres of which 1,741 acres are tideland regions. The bay contains cockle, gaper, soft-shell clams, crabs, perch, flounder, herring, salmon and oysters. The estuary is frequently dredged up to a distance of 14 miles inland to the town of Toledo. A pulp mill at Toledo disposes of its waste load out of the estuary by means of a pipe line to an ocean outfall.

Coos Bay contains approximately 9,543 acres of which 4,569 are classified as tidelands. Coos Bay is a major port with concentrated shipping, pulp processing, lumbering fish processing and other industrial activities. It is a water fowl area and an oyster, clam and crabbing area. Dredging, industrial pollution and filling of tidelands are important considerations for this area.

The Alsea contains approximately 2,227 acres within the bay. Major environmental changes have not yet occurred within this estuary. The principal changes may well be due to the logging activities within the upper regions.

Siletz Bay contains 1,203 acres. No major industrial activity is found in this region.

ECOLOGICAL CONSIDERATIONS

Aquatic ecosystems contain a wide variety of species. This diversity of species has been considered to be of great ecological importance, particularly in maintaining the stability of the ecosystem (2). Similar species compete for similar resources such as food, space and light. There is a tendency for the more efficient species to eliminate from the system the less efficient species (1).

Because a high species diversity is desirable, a question that should be asked with reference to water resource management is, "what are the environmental conditions which allow competitor species to coexist and how can these conditions be preserved?"

Environmental variations, both in time (68)(69)(70) and space (69)(71)(72) are major factors contributing to the coexistence of competitors and thus, the species diversity. Reduction of natural environmental variations can thus be expected to contribute to the reduction of species diversity.

Consider a cross section of a typical estuary as shown in figure 21. The estuary has been divided by the vertical solid line into two general sections: the main channel section (left side) and the tidal flat section (right side). These two sections have been further subdivided into four general regions. Regions A and A' consist of the main water bodies of each section. Regions B and B' are the water regions which extend several centimeters above the bottom. Vertical mixing in these regions is low and thus the chemical properties of regions B and B' are often quite different from the chemical properties of regions A and A'. The upper interstitial waters of the bottoms (waters containing dissolved oxygen) comprise regions C and C'. Deeper interstitial waters, lacking dissolved oxygen, make up regions D and D'.

Though varying in relative size, each of these eight general regions is of great ecological importance. Organisms which persist in one particular region would likely not survive in the remaining regions. Environmental conditions and variations with time are different for each of these regions. These differences are important as they contribute to the overall species diversity. (There are additional important variations within each of the defined regions, of course). Despite the ecological importance of all of these regions, water quality standards are written primarily for region A. Water quality monitoring by regulatory agencies is done almost exclusively in region A. Most research of water quality is concerned with region A. Most mathematical models involve only region A and occasionally region A'.

Thus, though all regions shown in figure 21 are ecologically important, most of these regions, particularly within the tidal flat section, have received little attention. Probably no other major sections of aquatic ecosystems have been so drastically changed by man's activities than the tidal flat areas.

To summarize, environmental differences in space and time are important as these differences contribute toward maintaining a high species diversity which, in turn, contributes toward an ecological stability. Natural tidal flats, therefore, are important to the estuarine ecosystem and to aquatic ecosystems in general because they are different.

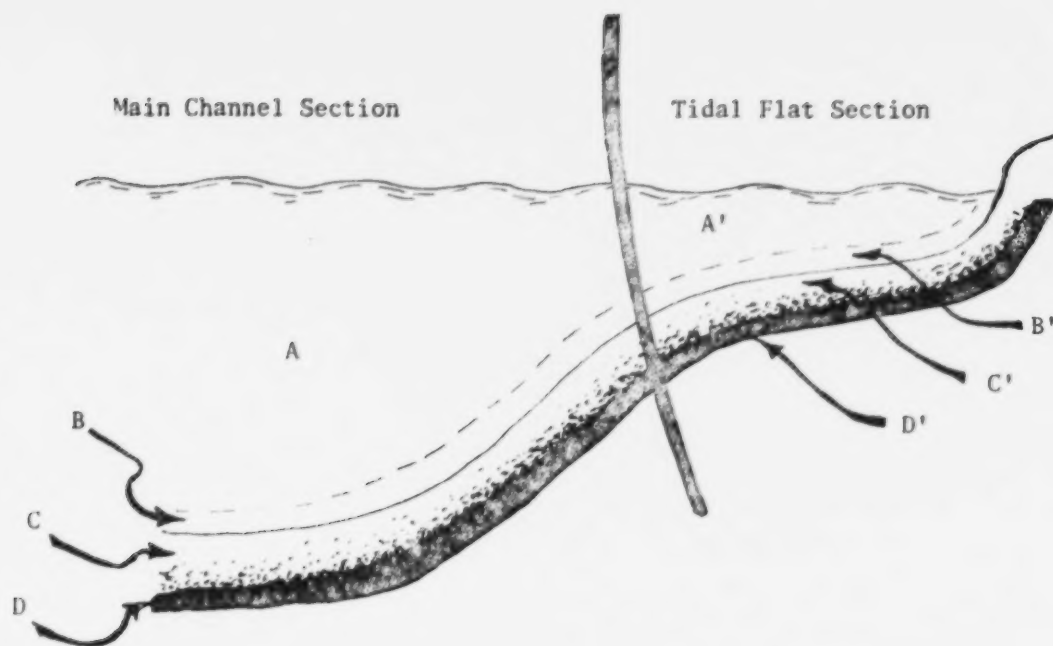


Figure 21 - Different Regions Within a Cross-section of
a Vertically Well Mixed Estuary

NATURE OF ESTUARINE DISPERSION

General.

The dispersion coefficient is a result of the one dimensional assumption used in equation 39. This assumption prevents the inclusion of velocity variations across a channel section. These velocity variations, have a tendency to spread water carried material along the channel length. This spreading is quantitatively expressed in the dispersion coefficient (along with the effect of turbulence).

Major differences between dispersion in rivers and estuaries result from the unsteady flow of estuaries and the density differences due to the salinity of estuaries. These two factors are briefly discussed below.

Effect of Unsteady Flow.

In a study of steady flow, Fisher (73) noted that the dispersion of a tracer from a point source may be divided into two time periods: (a) a convective period during which the tracer particle movements are dependent on their initial convective velocities, and (b) a later diffusive or "Taylor" period during which an equilibrium between longitudinal convection and cross sectional dispersion occurred. The dispersion equation was found to be applicable only during the latter "Taylor" period. The length of the convective period was found to be approximately six Lagrangian time scales. (The Lagrangian time scale is a measure of the time necessary for the motion of each tracer particle to be independent of its initial velocity).

It has been assumed that longitudinal dispersion in unsteady tidal flow is the same at each instant as for the corresponding steady flow. Such approaches also assume that the concentration distribution is in the Taylor state and that velocity profiles are identical to steady state profiles. In tidal flow, the hydraulic regime is continuously changing; thus, the "Taylor" state and steady state velocity profile may never be reached (74). This reasoning was based on estimations of the Lagrangian time scales that might be expected in Oregon estuaries. It was found that, for lateral variations, the Lagrangian time scales were substantially greater than the tidal period and thus, for lateral variations, the Taylor period would not be approached.

As lateral velocity variations are the major dispersive factors in steady flow conditions (73), it was reasoned (74) that one cannot

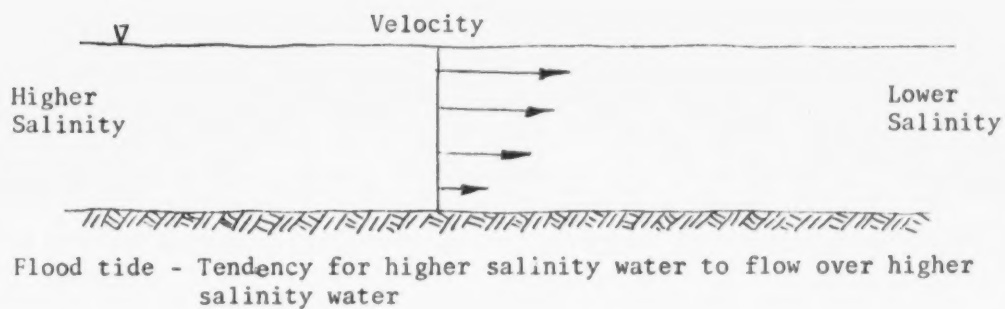
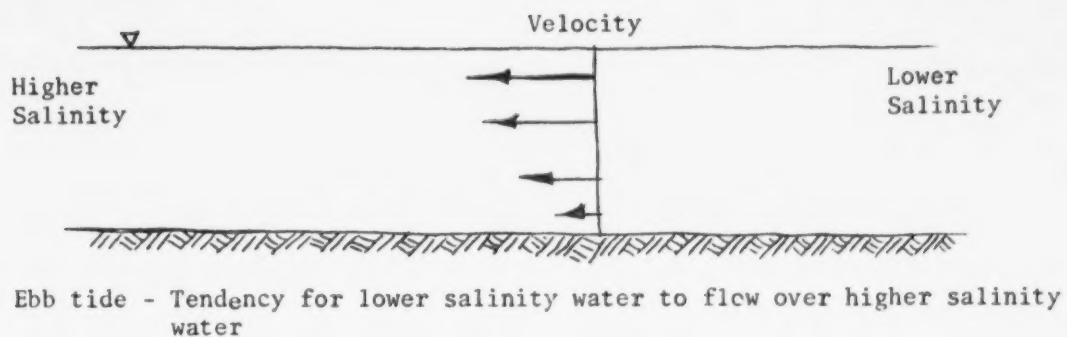


Figure 22 - Tendency for Vertical Salinity Change Over Tidal Cycle

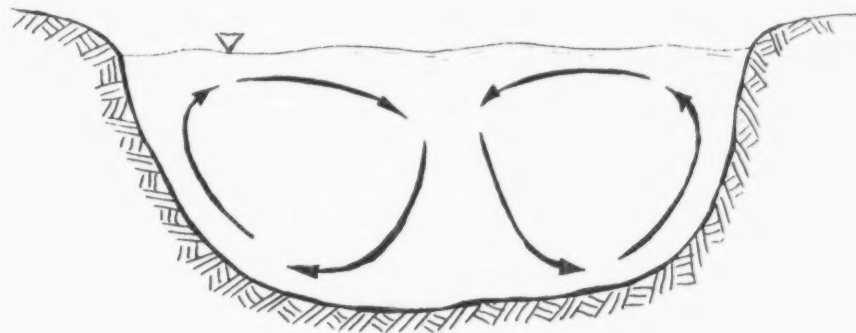


Figure 23 - Possible Secondary Currents During Flood Tide Within the Saline Region of a Relatively Narrow Tidal Estuary

assume that longitudinal dispersion in unsteady flow is the same at each instant as the corresponding steady flow. This problem has been independently pursued to much greater depth by Holley, Harleman and Fisher (75) and thus the reader is referred to this reference.

Some Effects of Density Differences.

The density differences within estuarine waters due to salinity differences have important effects on estuarine dispersion coefficients (76). Vertical stratification can lead to vertical Lagrangian time scales longer than the tidal period and thus, the "Taylor" state may never be approached, even for vertical variations.

A study of vertical and longitudinal salinity profiles suggests a further mechanisms involved in estuarine dispersion (within the saline region). Consider the simplified diagram shown in figure 22. Highest salinities are located in the seaward direction (left side of diagram). Assume that the estuary is completely mixed at high tide. As the water flows, in either direction, a vertical velocity gradient can be expected. Highest velocities can be expected within the upper region near the channel center. On the ebbing tide, the velocity gradients will tend to increase the vertical stratification. That is, at a given location, the salinity will decrease because the water is flowing from the less saline (landward) waters to the more saline (seaward) waters. The salinity will decrease most quickly in the regions of high velocity (upper-center region of the channel) because water transported to this region originated further upstream (due to the higher velocity). Thus, during the ebbing tide, vertical salinity gradients tend to increase due to longitudinal salinity gradients and vertical velocity profiles. Vertical turbulence will then tend to decrease these gradients.

Now, consider the condition during the flood stage of the tide. Assume that at the start of the flood stage, vertical gradients are present. Again assume that the high velocity region is located in the upper-center region of the channel. Now, by the same reasoning described above, the water velocities will tend to decrease the vertical gradients. If the riverflow is not too great, a condition can develop during the later period of the flood tide in which there is a tendency for the more saline water to flow over the less saline water. When this occurs, the heavier more saline water sinks to greater depths. In the narrower estuary channels, this overturning may thus contribute toward secondary currents in which downward velocities are found in the central high velocity regions while upward velocities are found in the low velocity regions near the shore (see figure 23). Thus, during the later portion of the flood tide, a density overturning may occur.

If the fresh water flow is high, the decrease in vertical gradients during the flood stage may not be sufficient to cause density overturning. It is suggested that the presence or absence of density overturning might be an effective means of classifying an estuary as either partially mixed or stratified.

A second related condition can also result. At the end of the ebb tide, the tendency to increase vertical gradients will decrease due to the decrease in the ebb velocities. The shallower depths during this period and during the low water slack period along with turbulence and drainage of tidal areas adjacent to the main channel may result in nearly complete vertical mixing during low water slack. Then, the tendency for density overturning would occur throughout the flood stage. Such a condition might serve to quantitatively define the difference between a well mixed estuary and a partially mixed estuary. The degree of mixing might be quantified by the fraction of the flood tide during which overturning occurs.

The dispersion coefficient found in such flow depends on all of the processes which occur over an entire tidal cycle. During the ebb stage, the velocity gradients spread the material along the length. Vertical diffusion and the density turnover during the flood stage prevent the material from realigning itself during the flood tide. It becomes difficult, therefore, to define a dispersion coefficient at a given location and at a given instant.

Transport of Floating Materials.

Secondary currents as shown in figure 23 would tend to move floating materials into the central-high velocity regions of the channel. If, due to overturning during the flood tide, these secondary currents were more prevalent during the flood tide than during the ebb tide, the net transport of floating material might well be in the landward direction. Within the Yaquina, a floating barrier had been constructed across the channel approximately 20 miles upstream. Large amounts of floating material collected on the downstream (seaward) side of this barrier. Floatable materials were often observed to be located within a narrow region along the channel center. Such floatables appeared to be moving upstream during the flood tide, in a line much like a convoy of ships. It is not known at this time how much overturning might contribute to such movements. Wind is no doubt an important factor.

MATHEMATICAL MODEL

General.

The general estuary model selected for this study is based on a one-dimensional finite-difference method (64). The stream channel is divided into cells of equal length (ΔX) and the content of each cell is analyzed during finite time increments (ΔT). Each cell is considered to be rectangular in shape with a cross sectional area equal to the average cross sectional area of that portion of the real channel which it represents.

For each time increment, the program begins at the fresh water end of the channel (the upper boundary) and calculates flows between each successive cell by means of the water quantity model. After flows have been calculated between all cells, the program returns to the upstream boundary and again proceeds down the channel, distributing pollutant concentrations by means of the water quality model. Time is then increased by one ΔT and the process is repeated. Tidal slough and tidal flat areas can be separately included within the model.

Water Quantity Model.

The upper boundary of the estuary was selected at a point where tidal flows became insignificant. A study of tidal hydraulics in the Yaquina Estuary was conducted during the first grant year. The results of this study have been published in a separate report (77). Analysis of this data is continuing under the sea grant program at Oregon State University. It is anticipated that this work will lead to a more basic water quantity than the one currently being used in this project.

Tidal heights along the estuary were determined in the model by methods similar to those developed for analytical solution to simple estuaries (78). However, numerical solutions to the differential equations were utilized in this study in order to include the irregular configuration of the Yaquina Estuary. The measured tidal wave was propagated up the estuary. The magnitude of the wave was changed with distance due to the frictional effects of the channel. It was assumed that the hypothetical upper boundary completely reflects the incident wave. The average water surface elevation in all cells for each time increment was determined by superimposing the height of the reflected wave onto the incident wave.

Channel cross sectional dimensions were obtained and cross sectional areas and stream widths were calculated for the mean water surface elevation. Algebraic functions were fitted to these data. The cross sectional area of each cell fluctuated with time about the mean value in accordance with the water surface elevation.

The changes in cross sectional areas can then be used to calculate average flows between cells over small time intervals, i.e. (average flow out of segment) = (average flow in) - (change in volume/ ΔT). A sensitivity analysis was conducted to determine the effect of grid parameter sizes (ΔX and ΔT) on the accuracy of this model.

Water Quality Model.

Convection and dispersion are considered to be the two mass transport mechanisms acting on each cell during each time increment. Each mechanism is calculated independently of the others in a multi-step process (64). This approach allows analysis of the relative effects of each factor and simplifies detection and correction of numerical errors.

Calculation of the convection of the pollutant between adjacent cells (N to $N+1$) in the main channel is accomplished by simple mass balance considerations. The mass of pollutant transferred between cells is equal to the volume of water which crossed the interface in time ΔT multiplied by the concentration in cell N and can be represented as:

$$\begin{aligned} C_{(N,T+\Delta T)} A_{(N,T+\Delta T)} \Delta X &= C_{(N,T)} A_{(N,T)} \Delta X \\ &+ UA_{(N,T)} C_{(N-1,T)} \Delta T \\ &- UA_{(N+1,T)} C_{(N,T)} \Delta T \end{aligned} \quad (40)$$

where $C_{(N,T)}$ is the concentration in segment N at time T , $A_{(N,T)}$ is the average area of segment N at time T , $UA_{(N,T)}$ is the average flow across the interface between cell N and cell $N-1$ during period ΔT , and cell $N-1$ is immediately upstream from cell N .

Because concentrations are considered uniform throughout each segment, a significant numerical error is introduced by this method of simulating convection. A careful investigation of this error was conducted (see reference(88)). The numerical spreading error was characterized by a pseudo-dispersion coefficient calculated by:

$$D_p = \frac{U}{2} (\Delta X - U\Delta T) \quad (41)$$

This error can be corrected in the dispersion step of the model by subtracting the pseudo-dispersion coefficient from the desired dispersion coefficient.

Dispersion describes the transfer of mass across cell interfaces caused by non-uniform cross sectional velocity gradients, and is represented in explicit finite-difference form as follows:

$$\begin{aligned} C_{(N,T+\Delta T)} &= C_{(N,T)} + F_1 C_{(N+1,T)} - C_{(N,T)} \\ &\quad + F_2 C_{(N-1,T)} - C_{(N,T)} \end{aligned}$$

$$F_1 = \frac{DA_{(n+1,T)} \Delta T}{A_{(N,T)} (\Delta x)^2}$$

$$F_2 = \frac{DA_{(n,T)} \Delta T}{A_{(N,T)} (\Delta x)^2} \quad (42)$$

where D = a dispersion coefficient which may vary with N and T and $A_{(n,T)}$ is the average of $A_{(N-1,T)}$ and $A_{(N,T)}$. A more complete description of the numerical models used in this study is given in reference (79).

SALINITY INTRUSION

General.

Salinity intrusion was simulated in a series of runs by holding the concentration at the mouth of the estuary constant at a value of 100. Usually after about 1500 real time hours, the salinity distributions in the estuary model began to repeat over each tidal cycle.

Although no attempt was made to completely model a specific estuary, the physical and tidal characteristics of the Yaquina Estuary at Newport, Oregon were used in the study. Cross sectional areas and widths at mean tide level were obtained at five stations along the estuary channel. Water surface elevations were recorded at the five stations during a complete tidal cycle on July 21, 1969. This tidal wave was utilized in the computer simulation. The end of the estuary was assumed to exist at a point 12,940 feet above the last station (Elk City) and data for this point was obtained by extrapolation of observed data.

For the finite difference representation, $\Delta X = 1320$ feet and $\Delta T = 15$ minutes were selected as practical grid parameters. Tidal variations about the mean were calculated for each cell at 15 minute increments for the tidal period. Values at each cell were obtained by linear interpolation of magnitude and time lag between stations where observed data was available. The sides of the channel were assumed vertical.

Determination of Dispersion Coefficients from Salinity Profiles.

Dispersion coefficients have been determined from steady state salinity profiles. (80)(81)(82). This approach assumes a balance between the seaward advective flux due to the fresh water flow and the landward flux due to longitudinal dispersion.

With the steady state assumption, the dispersion coefficient can be determined by equation 42,

$$D_L = \frac{QC}{A\Delta C/\Delta X} \quad (43)$$

in which Q is the net seaward flow and $\Delta C/\Delta X$ is the salinity gradient at a given location. The salinity gradients can be determined from profiles at various stages of the tide or they can be determined from profiles of salinities averaged over a tidal cycle.

When a steady state is not assumed, the following equation has been used.

$$D_L = \frac{QC + \Delta M/\Delta T}{A\Delta C/\Delta X} \quad (44)$$

$\Delta M/\Delta T$ is the rate change of total mass of salt upstream of the location of D_L . Different time periods may be used to determine $\Delta M/\Delta T$.

While equation (44) is an improvement over equation (43), a weakness of this equation lies in the determination of $\Delta C/\Delta X$. This value will vary with time. A method is developed below which reduces this weakness.

Consider a horizontal plane across the cross section of an estuary which moves up and down the estuary with the tidal current. The net seaward flow due to the river passes through this plane. The change in position of the plane is determined by the water velocity, U , minus the net seaward velocity. Thus, with identically reoccurring tides, the plane would return to the same locations with a period equal to the tidal period.

Considering the mass transfer across such a plane, one obtains

$$\int_{t_0}^t QC dt - \int_{t_0}^{t_1} D_L A \frac{\partial C}{\partial x} dt = M(t_0) - M(t_1) \quad (45)$$

in which $M(t_1)$ is the total salt mass upstream of the plane and A is the cross sectional area of the channel at the plane at a given time.

If the net seaward flow may be considered constant over the period $t_1 - t_0$, the first term of equation 45 can be reduced to

$$\bar{C} (t_1 - t_0) \quad (46)$$

in which $\bar{C}$ is the average concentration at the plane.

It must then be decided how one wishes to vary D_L within a tidal cycle. As previously discussed, the dispersion process results from a sequence of events which occur over at least an entire tidal cycle. It thus is difficult to define the dispersion coefficient closer than one tidal excursion. For the present,

consider D_L to be constant over the period $t_1 - t_0$. The second term in equation 45 then reduces to

$$-D_L \int_{t_0}^{t_1} A \frac{\partial C}{\partial x} dt \quad (47)$$

The gradient $\partial C / \partial x$ at the plane will vary with time. If the period, $t_1 - t_0$, is not great (generally not more than several tidal cycles), this variation will be due mainly to the temporal variation in A . When A is small, a given water body will be stretched out over a longer distance and thus $\partial C / \partial x$ will be small. Conversely, when A is larger, $\partial C / \partial x$ will be larger. As the longitudinal spread of a given water body will be linearly proportional to A , one may take

$$\frac{\partial C}{\partial x} = K^* A \quad (48)$$

or

$$K^* = \frac{1}{A} \partial C / \partial x \quad (49)$$

in which K^* is a constant which may be determined from measurements of A and $\partial C / \partial x$ during any portion of the period, $t_1 - t_0$. In estuaries in which density overturning occurs, samples taken during the overturning period are desirable due to the large reduction of vertical gradients.

Combining equations (45) (46) and (49) reduces equation (45) to

$$QC(t_1 - t_0) - D_L K^* \int_{t_0}^{t_1} A^2 dt = M(t_0) - M(t_1) \quad (50)$$

The integral in equation (50) may be found by plotting values of A^2 for a given plane and numerically integrating over the period $t_1 - t_0$. All other values, except D_L , may be determined from measurements taken at time t_1 and t_0 . The equation can then be solved to obtain D_L .

Comparison of Methods of Determining D_L .

A series of computer runs were conducted in which salinity profiles were computed as previously described. The dispersion coefficient was taken as $242 \text{ ft}^2/\text{sec}$ and the net seaward flow, Q , was taken as either 225 cfs or 50 cfs. Using the calculated salinity profiles, the dispersion coefficient was calculated by use of equations 43, 44 and 50. Results were then compared to the known dispersion coefficient used in the model.

For long runs in which the salinity profile repeated itself every tidal cycle, equation 43 and 44 became the same. In such cases, the calculated dispersion coefficients, using equations 43 and 44 and different methods of determining $\Delta C/\Delta X$, were usually within twenty percent of the known value. Values calculated from equation 50 were generally within five percent of the known values.

A series of runs were conducted in which the salinity profile was allowed to reach equilibrium at a given value of Q . Q was then either increased or decreased. The salinity profile then gradually shifted to a new equilibrium. During this period of equilibrium shift, equations 43, 44 and 50 were used to compute dispersion coefficients. The results of these runs are shown in Tables VI and VII.

The results show that equations 44 and 50 give reasonable results during this equilibrium shift with equation 50 generally giving the best results.

7
The results using equation 43 demonstrate the consequences of the steady state assumption. With this assumption, dispersion coefficients are underestimated when the salinity profile is shifting from a higher Q equilibrium to a lower Q equilibrium. An overestimate occurs when Q values are increased. Thus, if one were to determine dispersion coefficients with a steady state model from a record of salinity profiles and Q values, one would obtain a false relationship between Q and D_L . The assumption that transient conditions may be averaged out by developing profiles from many salinity measurements taken during different conditions of seaward flow (81)(82) is not warranted. Under such conditions, the salinity profiles at the higher flows will usually be shifting from the profiles developed with lower flows. Thus, an over estimate of D_L can be expected. Conversely salinity profiles at lower flows will usually be shifting from those found at higher flows and an underestimate of D_L can be expected.

It should not be implied that there is no relationship between Q and D_L . Glenne (83) found such an apparent relationship using an equation similar to equation 44. Use of the steady state assumption, however, will contribute toward a false relationship between Q and D_L .

TABLE VI. Dispersion coefficients (ft^2/sec) calculated during a shift in the salinity profile due to a sudden decrease in fresh water flow from 225 cfs to 50 cfs

Time (hrs)	3.8 miles from mouth			8.3 miles from mouth			15.2 miles from mouth		
	(a) Equa. 43	(b) Equa. 44	(b) Equa. 50	(a) Equa. 43	(b) Equa. 44	(b) Equa. 50	(a) Equa. 43	(b) Equa. 44	(b) Equa. 50
0	57.5	260.0	234.4	49.2	221.8	241.0	52.3	232.4	230.3
50	64.0	260.0	234.4	56.9	221.8	241.0	70.0	232.5	230.4
100	70.9	260.1	234.4	64.0	221.8	241.0	83.7	232.5	230.5
150	77.6	260.1	234.4	70.7	221.8	241.0	95.2	232.5	230.5
200	84.1	260.1	234.5	77.2	221.8	241.0	105.3	232.6	230.5
300	96.7	260.1	234.5	89.8	221.8	241.0	122.4	232.6	230.5
400	108.8	260.1	234.5	101.6	221.8	240.9	137.0	232.6	230.5
500	120.4	260.1	234.5	112.7	221.8	240.9	149.6	232.6	230.5
600	131.6	260.1	234.5	123.1	221.8	240.9	160.5	232.6	230.5
700	142.3	260.2	234.5	132.7	221.8	241.0	170.1	232.7	230.6
800	152.4	260.2	234.5	141.7	221.8	241.0	178.4	232.7	230.6
900	162.0	260.2	234.5	150.0	221.8	241.0	185.7	232.7	230.6
1100	179.6	260.2	234.6	164.5	221.8	241.0	197.5	232.8	230.7
1200	187.5	260.2	234.6	170.8	221.8	241.0	202.2	232.8	230.7
1300	194.8	260.2	234.6	176.6	221.8	241.0	206.3	232.8	230.7
1400	201.5	260.2	234.6	181.7	221.8	241.0	209.9	232.8	230.7
1600	213.4	260.2	234.6	190.5	221.9	241.0	215.6	232.9	230.8
1800	223.2	260.2	234.6	197.5	221.9	241.0	219.8	232.9	230.8
1975	230.3	260.3	234.7	202.4	221.9	241.0	222.7	232.9	230.8

(a) Salinity gradients based on the profile at the time of high water slack at the mouth.

(b) Salinity gradients averaged from the profile at the beginning and end of the tidal cycle at the time of high water slack at the mouth. Change in mass measured over the same period.

TABLE VII. Dispersion coefficients (ft^2/sec) calculated during a shift in the salinity profile due to a sudden increase in fresh water flow from 50 cfs to 225 cfs

(hrs)	3.8 miles from mouth			8.3 miles from mouth			15.2 miles from mouth		
	(a) Equa. 43	(b) Equa. 44	(b) Equa. 50	(a) Equa. 43	(b) Equa. 44	(b) Equa. 50	(a) Equa. 43	(b) Equa. 44	(b) Equa. 50
0	1039.7	260.3	234.7	912.3	221.9	241.1	999.9	234.0	232.0
50	942.2	260.2	234.6	772.8	221.8	240.9	676.9	234.1	232.0
100	844.1	260.2	234.5	644.9	221.9	241.0	474.1	234.7	232.6
150	754.3	260.2	234.5	537.5	221.9	241.1	373.0	234.9	232.8
200	671.9	260.2	234.5	455.5	221.9	241.1	322.8	234.9	232.8
300	534.2	260.2	234.6	356.2	221.1	241.2	278.9	234.9	232.8
400	437.9	260.2	234.6	306.1	221.1	241.2	261.0	234.9	232.8
500	375.8	260.2	234.5	278.1	222.2	241.3	252.1	234.9	232.8
600	336.4	260.2	234.5	260.7	222.2	241.3	246.9	234.9	232.8
700	311.1	260.1	234.5	249.2	222.2	241.4	243.5	234.9	232.8
800	294.6	260.1	234.5	241.2	222.2	241.4	241.2	234.9	232.8
900	283.7	260.1	234.5	235.6	222.2	241.4	239.4	234.9	232.8
975	277.9	260.2	234.5	232.6	222.2	241.4	238.5	234.9	232.8

(a) Salinity gradients based on the profile at the time of high water slack at the mouth.

(b) Salinity gradients averaged from the profile at the beginning and end of the tidal cycle at the time of high water slack at the mouth. Change in mass measured over the same period.

DISPERSAL OF POLLUTANTS

General.

Studies using numerical methods have shown that, with several exceptions, the pollutant profiles determine from equation 39 are far more sensitive to K_1 than to D_L . Only when high concentration gradients are present is the profile more sensitive to D . High concentration gradients occur for the following conditions.

1. A pollutant slug is placed into an estuary.
2. A continuous pollutant source has a variable strength. Concentration peaks result during times of high pollutant output.
3. A continuous pollutant source in an estuary has a relatively constant strength. A concentration peak is formed during periods of slack water.

Conditions 2 and 3 can combine to form higher peaks than would occur with either condition alone. Condition 3 leads to the formation of a concentration peak during each slack water. Such peaks have been considered with reference to thermal waste heat in the Columbia River (84).

In the following sections, slack water concentration peaks at pollutant outfalls (condition 3) are examined through a field study and a mathematical model.

Field Study.

Elk City is located near the fresh water end of the Yaquina Estuary approximately 22.5 miles (36.2 km) from the mouth. The study area was a fairly regular seven mile (11.3 km) section of channel without intersecting tributaries, extending towards the mouth from Elk City to Mill Creek. A diffuser was constructed by placing six nozzles at equal spacing on a 150 foot (46.2 m) length of half inch (1.27 cm) diameter plastic irrigation pipe. The nozzles were adjusted to provide equal flow rates and then the diffuser was installed across the estuary channel approximately one mile (1.6 km) from Elk City. The diffuser was anchored to the bottom by concrete blocks, and floats were attached in order to hold the nozzles about one foot (0.3 m) above the bottom. Water was pumped into the diffuser at a rate of about 20 gallons per minute (75.6 liters per minute). A concentrated solution of rhodamine -B dye was injected into the diffuser at a nearly constant rate of 68.1 grams per hour for 12 hours.

Water surface elevations were continuously measured with Stevens automatic tide recorders at Elk City and at Mill Creek. Observed data are shown in figures 24 and 25 respectively. Water surface elevations measured at the diffuser are shown in figure 26.

Velocities were measured with a Price current meter at four depths near each of the quarter points of the stream width near the diffuser. An arithmetic average of the 12 velocity measurements was assumed to represent the average cross sectional velocity. Observed data are shown in figure 27. After 21:00 hours, velocity measurements were taken only at the channel centerline.

Samplers were constructed by attaching rubber bulbs at two foot (0.6 m) intervals on poles which were 12 feet (3.6 m) long. Air was expelled from each bulb by squeezing and then a plug was inserted in the end. Samples could be obtained simultaneously at several depths, therefore, by inserting the pole vertically in the water and removing the plugs by means of an attached cord which extended to the surface. Each bulb would draw in a water sample of about 75 ml. Water was then expelled from the bulbs into glass bottles for later evaluation. Laboratory investigations prior to the field study indicated that the rubber bulbs would have no significant influence on the rhodamine -B concentration in the water samples.

Buoys were set to divide the stream width into quarters at the diffuser and at a seaward section located 235 feet (72.4 m) from the diffuser towards the mouth of the estuary. Water samples were taken at points approximately five feet (1.5 m) downstream from each of the buoys at the diffuser section every half hour or as determined necessary. Samples were also taken every half hour near the buoys at the seaward section.

Each sampling run consisted of taking four to seven vertical samples at each of the buoys. A sampling run would take between five to ten minutes to accomplish. All of the sample concentrations from each run were averaged in order to obtain the average cross sectional concentrations and these values are plotted in figure 28a. Thus over 400 individual samples were utilized to obtain the data represented in figure 28a. Due to fog and other field difficulties after dark, samples were taken only at the channel centerline after 21:00 hours. When more than one series of vertical samples was taken during the same ten minute period, all values were averaged to obtain the average cross sectional concentrations. The standard deviation calculated from the data of each run are plotted in figure 29.

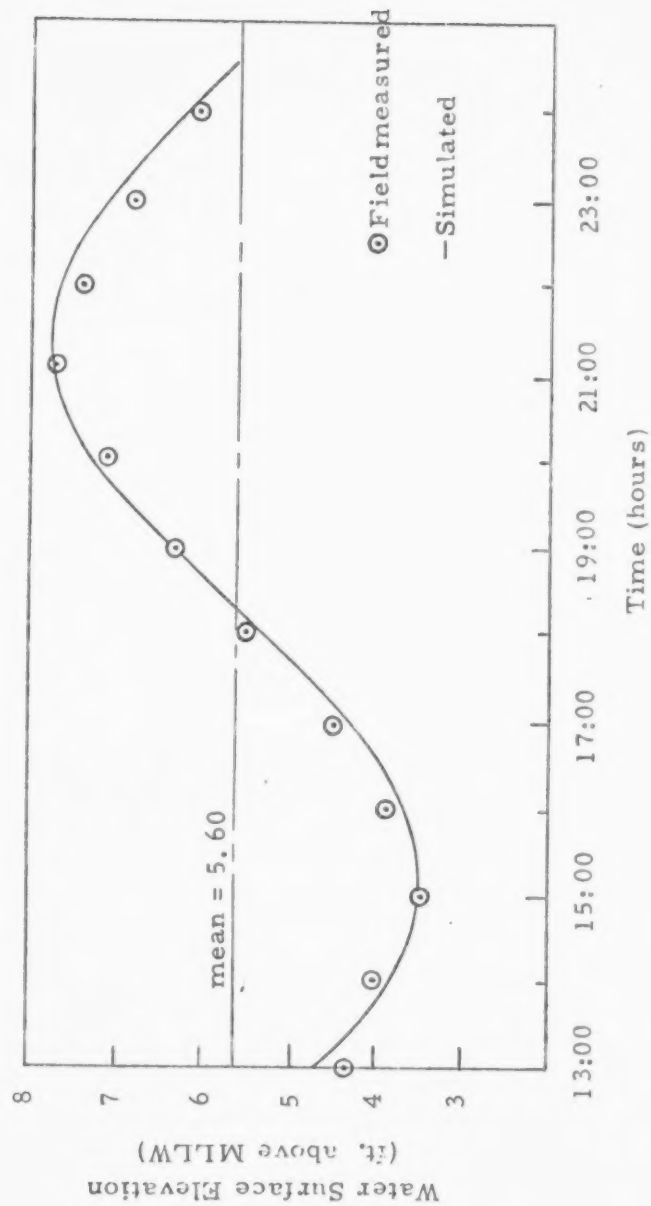


Figure - 24. Water Surface Elevations at Elk City.

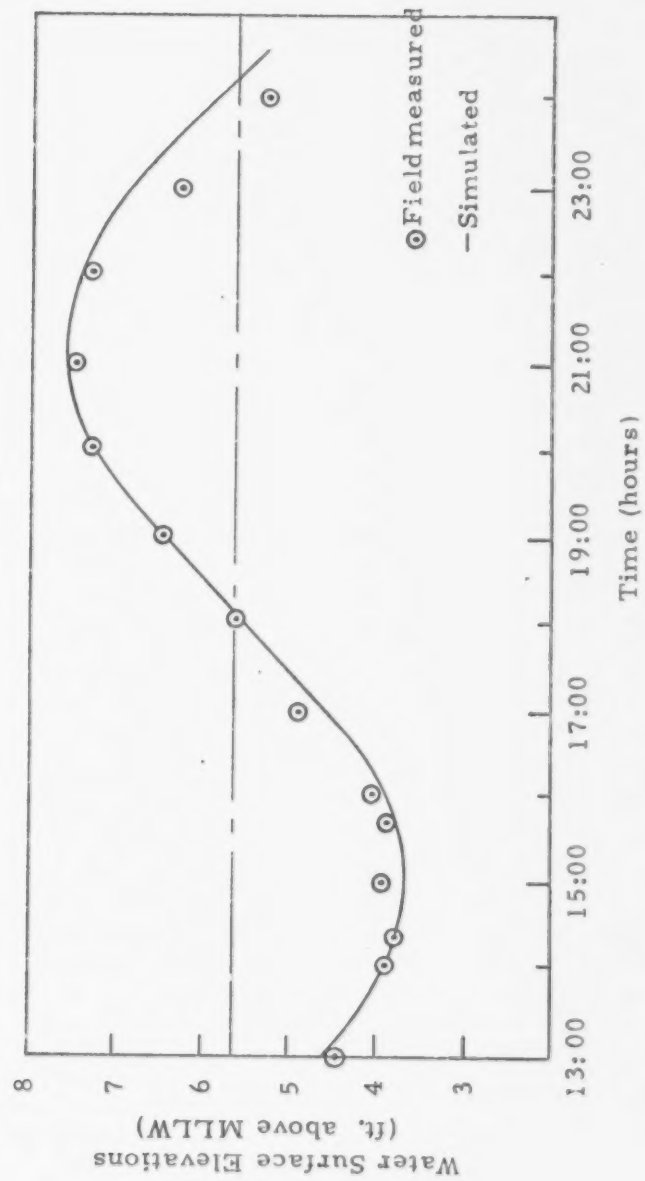


Figure - 25. Water Surface Elevations at Mill Creek.

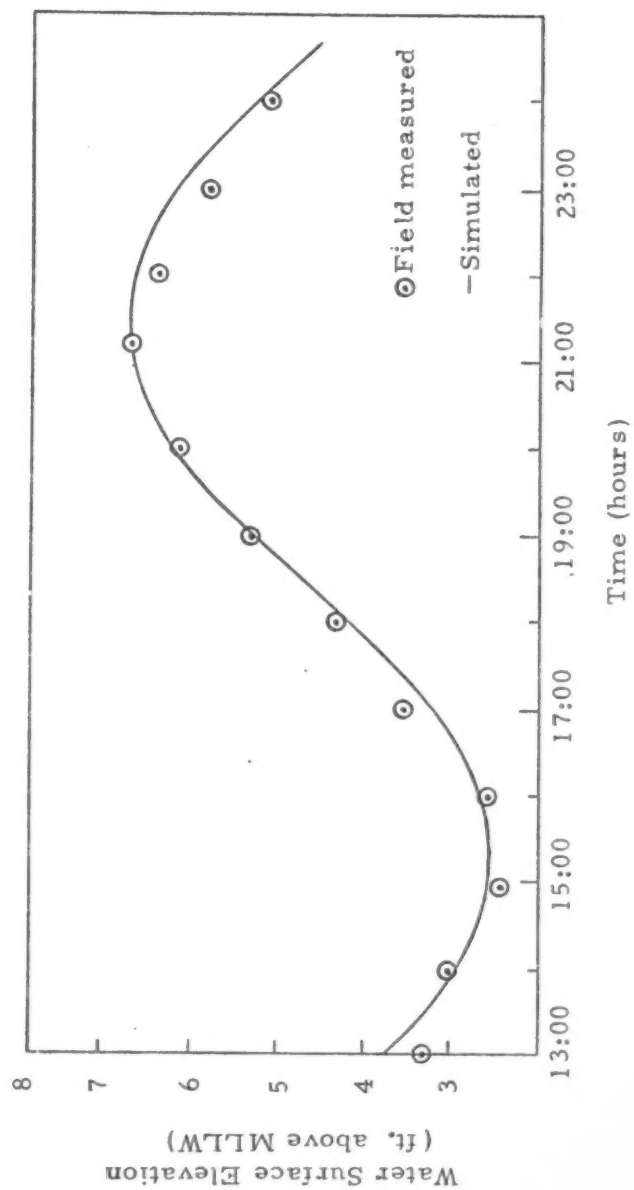


Figure - 26. Water Surface Elevations at Diffuser.

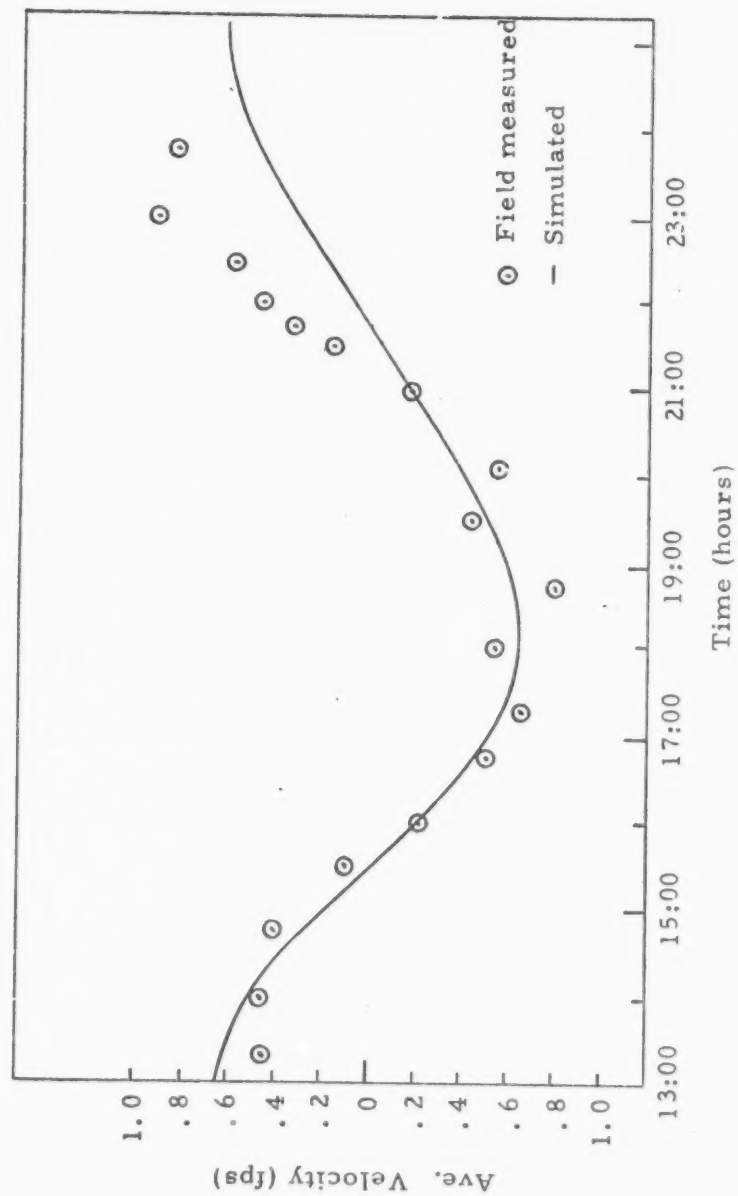


Figure - 27. Average Cross-Sectional Velocities at Diffuser Section.

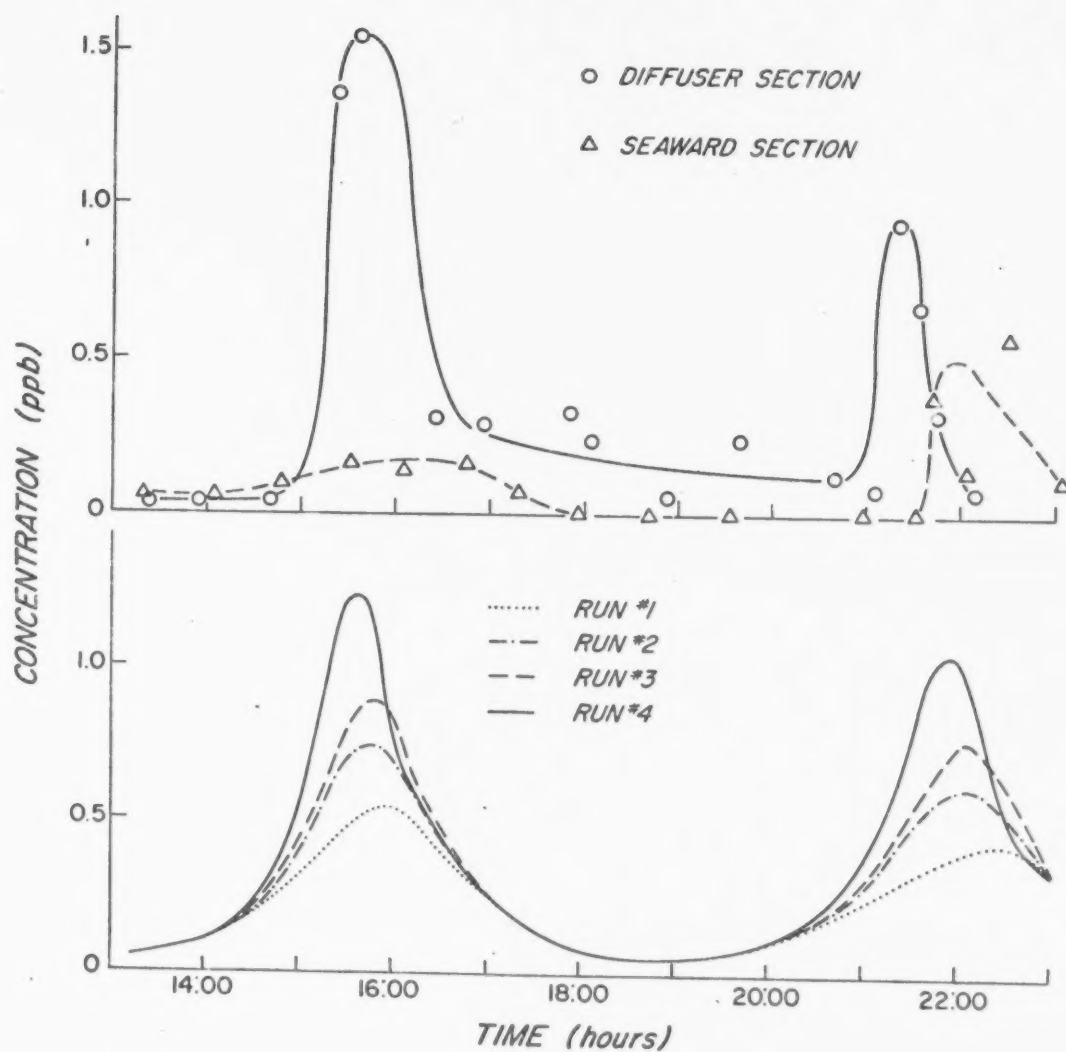


Figure - 28. Average Cross-Sectional Concentrations; (a) Field Observed and (b) Mathematical Model Results.

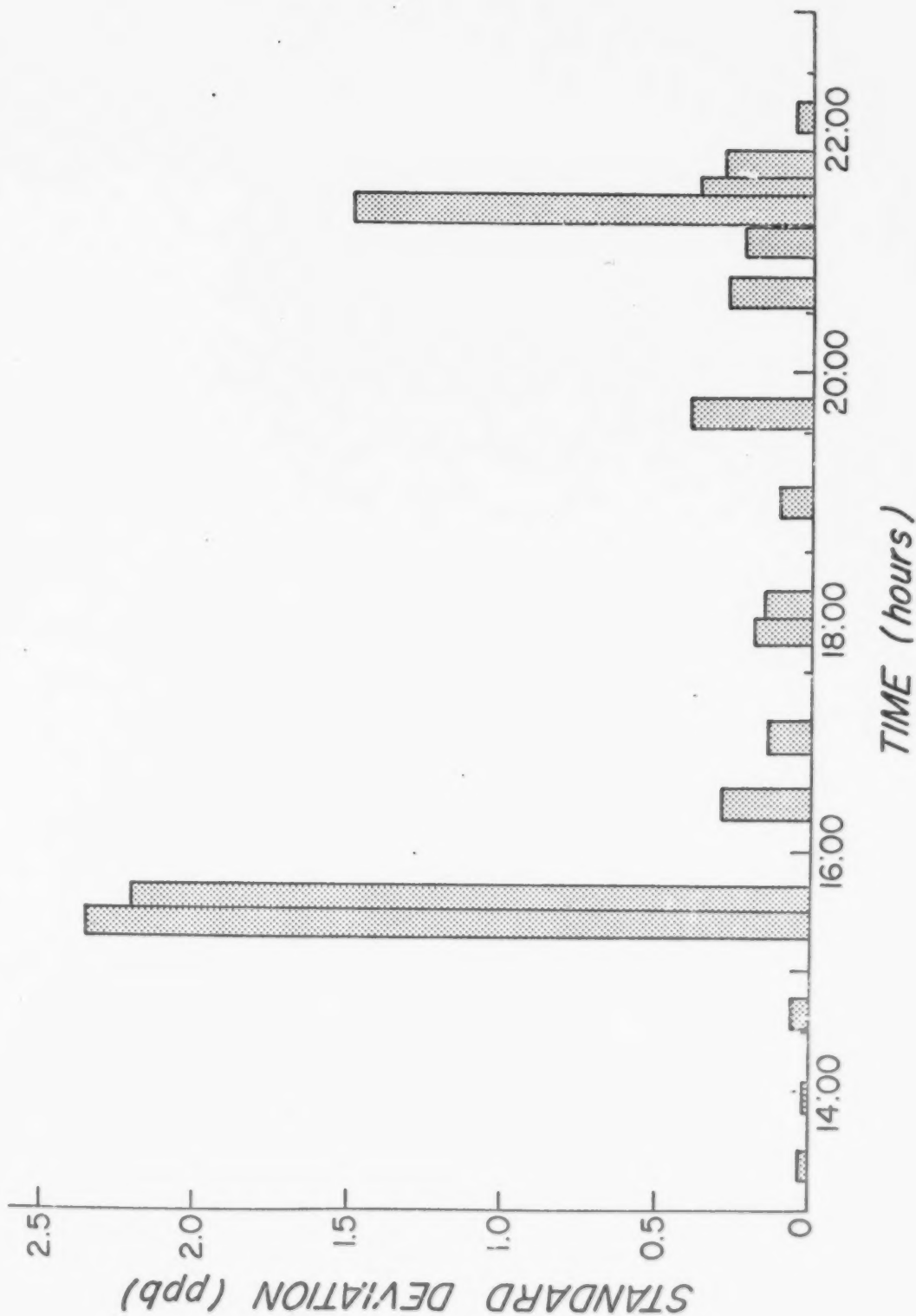


Figure - 29. Standard Deviations of Field Samples.

Mathematical Model Study.

The mathematical model previously described was utilized to compute the tracer profiles. The model was fitted to measured tidal elevations. (see figures 24, 25 and 26). Fresh water flow was negligible during the study period so zero flow was specified at the upper boundary of the model. The water velocities at the diffuser which were simulated by the model are shown in figure 27. The observed average cross sectional velocities during ebb tide between 13:00 and 15:00 ranged from 83.5% to 93.7% of the velocities at channel center. The departure of the model from the prototype in figure 27 may be partially explained by the fact that velocity measurements were taken only at the channel center after 21:00 hours and, therefore, are higher than the average cross sectional velocities represented by the model.

No values for the dispersion coefficient (D), as defined in this model, were available for the Yaquina Estuary. Therefore, several computer runs were conducted using different values for comparison. Run number one (figure 28b) was conducted using a constant dispersion coefficient equal to 75 ft²/sec (6.97 m²/sec). Run number two (figure 28) used a dispersion coefficient which varied as a linear function of the velocity:

$$D = 20 + 133 |\text{velocity}|$$

The maximum value for this variable dispersion coefficient was selected so that the area under the curve defined by the variable coefficient (see figure 30) would equal the area under the line defined by the constant dispersion coefficient of run number one.

Run number three (figure 28) used a variable dispersion coefficient defined by:

$$D = 50 |\text{velocity}|$$

This function is similar in form and magnitude to dispersion coefficients used in models of the Potomac Estuary (85).

Run number four (figure 28b) used the same D as run three, but grid parameters were cut in half so that $\Delta X = 0.05$ miles (80.5 m) and $\Delta T = 1/12$ hours.

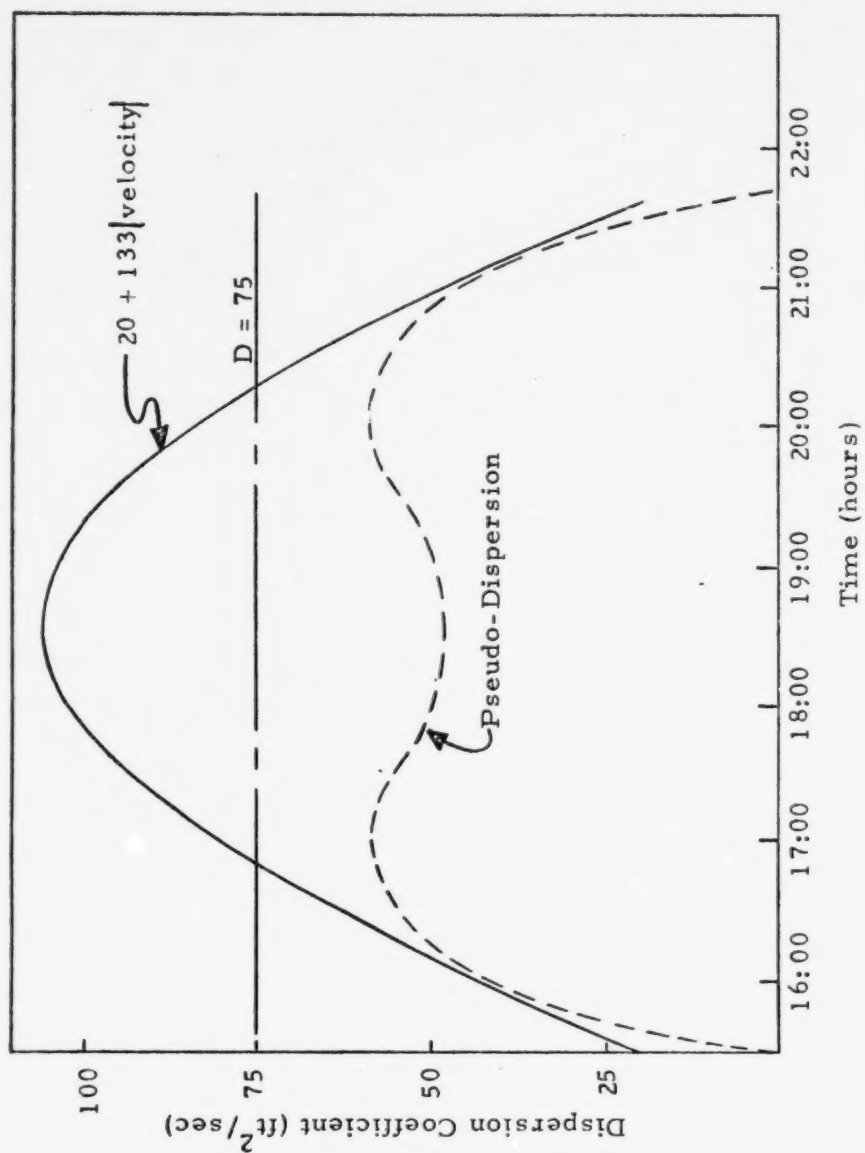


Figure - 30. Dispersion Coefficients For One Half of a Tidal Cycle at the Diffuser.

Discussion.

Field observations showed a significant build up of tracer concentrations over the outfall during slack water. The peaks of the average cross-sectional concentrations shown in figure 28a are from five to nine times as large as the concentrations one half hour before the slack. Although data is less reliable at high slack, due to the reduction in sampling points after 21:00, this relationship is logical because of the larger cross-sectional water area at high slack. A peak does not appear in figure 28a at the section seaward from the outfall at low slack because the concentration buildup was washed up the estuary by the flood tide.

Some of the individual sample concentrations exceeded the peak average values by as much as 400 percent. The non-uniform distribution of the tracer was observed in the field during low slack when concentrations at some points were sufficient for the rhodamine-B to become visible. The individual sample concentrations were widely scattered as indicated by the high standard deviations plotted in figure 29. The highest variances are seen to occur in conjunction with high concentrations. This would be expected because of the greater range of possible sample values. The coefficients of variation were calculated for each point in figure 29 and the average of these values was 0.68. This wide scatter of individual sample concentrations indicates that the estuary is not completely mixed across the cross section in the vicinity of the outfall and demonstrates the necessity for thorough sampling procedures in field studies of this type.

The mathematical model results, shown in figure 28b, resemble the general trend of the observed data. The two slack water peaks are apparent with the higher one occurring at low slack. The influence of the dispersion coefficient in the model when steep concentration gradients are encountered is demonstrated by comparing runs 1, 2, and 3 in figure 28b. The constant D in run 1 results in a relatively flat peak compared to the results from a variable D in run 2. When the magnitude of the variable D is increased the peak concentrations are further increased (run 3).

The concentrations from the simulated runs consistently underestimate the observed values at the outfall (figure 28). This trend is readily explained by the fact that the finite-difference representation in the model calculates values averaged over a distance ΔX . If the grid parameters (ΔX and ΔT) of run 3 are reduced by 50 percent, the results indicate a 37 percent increase in the peak concentration as shown by run 4 in figure 28b. If the values of run 4 are averaged over two ΔX segments, a curve similar to run 3 is obtained. Thus, when ΔX is reduced from 1/10 mile (0.161 km) to 1/20 mile (0.080 km) the average concentration over 1/10 mile

(0.161 km) does not necessarily change, but the concentrations in two adjacent cells may vary considerably about this mean. The concentration peaks calculated by the model are, therefore, sensitive to both the dispersion coefficient and the size of the grid parameters.

When a moderate fresh water flow was introduced into the mathematical mode at the upper boundary, individual peaks were produced and convected seaward by the net seaward water velocity. These peaks, however, were not as distinct as the ones described by runs 2, 3 and 4 above because they were transported back and forth across the outfall until the net seaward convection exceeded the tidal excursion. Because the net seaward velocity decreased as the channel area increased, the peaks merged into a uniform concentration a few miles seaward of the outfall.

The case of a uniform channel with river flow predominating over tidal fluctuations was also simulated. When the river flow was of sufficient magnitude to allow only slight tidal reversal at the outfall, a concentration peak would build up during each slack water. These peaks would then be dispersed as they moved downstream. Such peaks were most significant when the river flow was sufficient to result in little or no tidal reversal. Maximum concentrations at the outfall generally reached 3 to 5 times the values calculated when only river flows were considered and tidal flows were neglected.

CHANGES IN ESTUARINE SEDIMENTS

In chapter II, the release of sulfides to the upper regions of the deposits and to the overlying water was found to depend to a large extent on the vertical mixing within the deposits. Lower vertical mixing, in turn, was found to be closely related to larger amounts of fine particles within the deposits.

In the introduction of this report, the possible effects of dams and dredging on estuarine sediments was briefly discussed. During the next (last) grant year, the relationship between particle size and free sulfide concentrations will be studied in greater depth. In addition, long term records will be reviewed to see if a significant decrease in particle size can be related to man's activities. A significant long term decrease in particle size within a developed estuary has been recently reported (86).

It is recognized that an in depth study of estuarine sediment changes resulting from a variety of man's activities cannot be completed within the final year of this project. It is hoped, however, that during the final year of this study, a more complete definition of these changes and their possible consequences might be obtained.

Such results might then encourage meaningful research beyond the scope of this project. In addition, research conducted under this project should provide tools for such a study. As an example, the estuarine water quantity-quality models can be used for the description of salinity profiles.

The net landward velocity of bottom estuarine waters in well mixed and partially mixed estuaries is related to the salinity profile (87). Thus, sediments are often transported inland. A study of net bottom velocities and their effect of shoaling is currently being initiated under the Sea Grant Program (NSF), Ocean Engineering, Oregon State University. Close cooperation with this study is anticipated.

SOURCES OF ORGANICS

As discussed in Chapter II, the organic content of tidal flat deposits is an important consideration. Such organics may be introduced into the estuarine system from outside sources (such as industrial and domestic waste sources) or result from primary production within the estuary. Primary production, both benthic and planktonic, is likely a major source of organics, which are introduced into tidal flat systems.

During the last grant year of this project, the estuarine water quality models will be expanded to include primary production. This portion of the study will work closely with an experimental project being conducted within the Department of Oceanography, Oregon State University.

CHAPTER IV

SUMMARY

During the second grant year, emphasis was given to the study of the tidal flat system. Respirometer data from the previous grant year was analyzed and further in situ respirometer studies were conducted.

Based on field studies and literature review, a conceptual model of the tidal flat system, which emphasized the sulfur cycle, was developed. A mathematical model describing the diffusion and oxidation of oxygen demanding materials within the upper regions of the benthic deposits was developed. Under certain conditions, free sulfide concentrations within the tidal flat waters were measured at concentrations of approximately 1 mg/l even within water containing 4 mg/l or more of dissolved oxygen. The literature indicates that such free sulfide levels can be quite harmful to a wide variety of desirable species. Measured free sulfide concentrations fell within the range of calculated estimates. The presence of silt and clay particles and organics within the deposits, shallow water depths, available sulfates, low DO concentrations, poor drainage and low water velocities were described as conditions favoring higher free sulfide concentrations within the overlying waters.

A more complete preliminary model of the benthic system has been developed. Laboratory and field experiments have recently been initiated in order to refine the model, investigate the assumptions, and define the parameters more closely.

A finite-difference estuarine water quality model was developed. Significant finite-difference errors were studied and means of controlling these errors were developed. Pollutant slack water accumulation at continuous outfalls were studied both through a field experiment and through a mathematical model study. An improved method of determining the longitudinal dispersion coefficient from longitudinal salinity profiles was developed. Mathematical model studies demonstrated that calculations of dispersion coefficients using salinity profiles and models which assume a steady state lead to a false relationship between the fresh water inflow and the dispersion coefficient.

During the next grant year, the estuarine models will be expanded to include primary production. Changes of estuarine sediments and the consequences of such changes will also be studied.

APPENDIX I

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APPENDIX II

PUBLICATIONS SUPPORTED BY THIS PROJECT

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